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Volume 27 April 1, 1944 Number 4

CASTING CHARACTERISTICS OF CLAYS: I, IMPROVED METHODS FOR DETERMINATION*

By R. Russell, Jr., and W. C. Mohr

Abstract

Part I of this investigation covers the development of reliable laboratory tests to indicate the relative properties of different clays with the primary consideration of their casting behavior. Methods are given for the determination of casting rate, permeability, water retention, fluidity, thixotropy, organic content, shrinkage, and dry strength. By determining the effect of varying increments of electrolyte on the foregoing properties, it is possible to select clays which have desirable casting characteristics for commercial use. Samples of fast- and slow-casting kaolins and ball clays were used to indicate the utility of the methods employed; results are also given for two composite bodies. In developing the test procedures using the Büchner funnel (vacuum), the effect of the following factors was determined: mixing procedure, ratio of clay to flint, feldspar vs. flint as the nonplastic, electrolyte content, quantity of slip used, specific gravity of slip, slip temperature, aging, and vacuum pressure; The optimum procedure for testing clays was then evolved. Part II and Part III of this series of studies are in preparation for publication.

I. Introduction

A development of improved casting compositions for the manufacture of high-tension electrical porcelain and the substitution of domestic for imported clays in these bodies brought to attention the fact that there is an insufficiency of comparative information on the casting properties of commercial whiteware clays. Owing to this paucity of data, too many casting body developments have been conducted on a trial-and-error basis. Many informative reports, however, have been made on casting clays and methods of test. The present investigation seeks to assemble the more valuable existing tests and to combine these with new and improved methods to produce an organized and systematic procedure for developing of a casting body.

Hall,[1] in a résumé of the literature to 1930, emphasized the importance of clay properties and the necessity for proper clay selection and proportioning in the development of casting bodies. The influence of these factors is recognized, and various methods of determining the most important properties have been suggested. Schramm and Hall[2] have discussed the importance of water movement and water retention, and the effects of such factors as temperature, aging, specific gravity, and viscosity of slip. Wills[3] interpreted the effect of eleven slip properties in terms of production losses and described two types of specimens for trial casting-rate tests (thickness in leather-hard and dry states was determined). He concluded that losses increase with abnormally high or low viscosity slips and that unusual reductions in casting time cause high losses in drain casting. Klinefelter and his co-workers[4] reported the properties of domestic kaolins and English china clays without particular consideration for their casting properties, but they observed deflocculation characteristics and fineness as indicated by colloidal content (<0.6 micron) which are important properties in determining casting behavior.

Hall[5] suggested the use of the Bingham plastometer for determining the consistencies of slips and the relative plasticities of clays. Using this plastometer, Fritz and Donnenwirth[6] were able to determine the relative casting properties of clays but stated that

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (White Wares Division). Received January 10, 1944.

[1] F. P. Hall, "Casting of Clayware, a Résumé," *Jour. Amer. Ceram. Soc.*, **13** [10] 751–66 (1930).

[2] E. Schramm and F. P. Hall, "Notes on Casting Slip," *ibid.*, **17** [9] 262–67 (1934).

[3] G. A. Wills, "Notes on Casting Slip in Production," *ibid.*, **15** [2] 130–34 (1932).

[4] (*a*) T. A. Klinefelter, W. W. Meyer, and E. J. Vachuska, "Some Properties of English China Clays," *ibid.*, **16** [6] 269–76 (1933).

(*b*) T. A. Klinefelter and W. W. Meyer, "Properties of Some American Kaolins and a Comparison with English China Clays," *ibid.*, **18** [6] 163–69 (1935).

[5] F. P. Hall, "Methods of Measuring Plasticity of Clays," *Bur. Standards Tech. Paper*, No. 234, 22 pp. (March 22, 1923).

[6] E. H. Fritz and A. L. Donnenwirth, "Some Observations in the Casting of Heavy Electrical Porcelains," *Jour. Amer. Ceram. Soc.*, **8** [9] 547–54 (1925).

serious variations in production bodies were sometimes not indicated. This method of test seems to have definite limitations. Shearer[7] described the R & S plastometer for testing clay and body slips and indicated its usefulness for measuring slip plasticities, for determining complete slip deflocculation, and for comparing the effects of different electrolytes, but this method has not found general use in clay testing.

Wilson and Page[8] developed a simple test to compare the degree of dispersion of different clays during blunging. This test might indicate the extent of blunging treatment necessary in the production use of clays.

Numerous methods have been developed for the determination of slip viscosity, but the Marriotte tube or flow-type viscosimeter[9] or a modification thereof has been most widely employed. The MacMichael[10] viscosimeter, as used by Speil[11] and by Norton and Johnson,[12] was reported to be simple in operation and to cover a wide range, yielding precise results even at low viscosities. Henry and Taylor[13] favored the Stormer viscosimeter because of its flexibility and ease of operation, and Sproat, Treischel, and Emrich[14] used this viscosimeter successfully to determine the thixotropic tendencies of casting slips. The latter investigators used a flow-type viscosimeter for viscosity tests, and both the cup and disk casting-rate tests (wet weight) in the study of casting bodies compounded from domestic clays. The Gardner mobilometer[15] was used by Carter and King[16] to determine the effect of a special electrolyte on casting slips.

The Irwin consistometer described by Irwin and Bevis[17] was used successfully by Loomis[18] to show the effect of aging on the consistency of casting slip. Loomis also conducted cup casting-rate (dry weight), water-retention, grain-size, and pH tests on casting slips. He concluded that the percentage of material finer than 1.0 micron can be used as an important criterion in determining casting rate and that hydrogen-ion measurements may be used advantageously to control casting slips. Phelps[19] used a casting-rate test in which a conical cup was cast and the dry thickness was determined for three casts of 5, 10, and 20 minutes each.

Earhart[20] investigated casting slips, using a flow-type viscosimeter and a cup casting-rate test (dry weight). He found that a body of almost any desired casting quality may be compounded if the properties of individual clays are known.

A permeability test for casting clays, using a Büchner funnel and vacuum, was described by Harman.[21] This same equipment has been used in a simulative test[22] to determine the casting rate of a whiteware body. A similar test was first suggested by Hall.[1]

The foregoing search of the literature showed that there is no general agreement between investigators as to the selection of test methods which will indicate the properties of casting clays, although there is some concurrence of opinion such that slip properties as fluidity (viscosity, consistency, and plasticity), casting rate, and water retention are important limiting factors.

There is also a lack of complete information permitting comparisons between the clays available, and in only one case was there any deliberate attempt to compound casting bodies on the basis of tests on individual clays.[20(d)] An attempt has been made in the present paper to develop and use a sufficient number of practical test methods to permit an evaluation of all properties which are important in the casting usage of clays and body slips.

This first report describes the test methods used and the various controlling factors. Test results are also given for four clays and two bodies to indicate the usefulness of the methods.

II. Test Methods

It was necessary to decide which properties of a clay or body slip would adequately describe its casting character. Preference was given to fluidity (viscosity, consistency, plasticity), thixotropy, casting rate, permeability, water retention, organic content, shrinkage, and dry strength. Particle size and shape, soluble salt content, hydrogen-ion concentration, exchangeable bases, and chemical and mineralogical

[7] W. L. Shearer, "Control of Plasticities of Ceramic Slips," *Jour. Amer. Ceram. Soc.*, **15** [11] 622–29 (1932).

[8] Hewitt Wilson and G. A. Page, "Simple Dispersion Test for Clays," *ibid.*, **16** [2] 82–85 (1933).

[9] (*a*) H. G. Schurecht, "Relation of Salt to Clay in Purification of Clays," *Trans. Amer. Ceram. Soc.*, **19**, 460–78 (1917).

(*b*) A. V. Bleininger and M. R. Horuung, "Notes on Casting," *ibid.*, **17**, 330–55 (1915).

[10] R. F. MacMichael, "Testing of Clay," *ibid.*, **17**, 639 (1915).

[11] S. Speil, "Effect of Adsorbed Electrolytes on Properties of Monodisperse Clay–Water Systems," *Jour. Amer. Ceram. Soc.*, **23** [2] 33–38 (1940).

[12] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: II, Mechanism of Deflocculation in the Clay–Water System," *ibid.*, **24** [6] 189–203 (1941).

[13] E. C. Henry and N. W. Taylor, "Acid and Base Binding Capacities and Viscosity Relations in Certain Whiteware Clays," *ibid.*, **21** [5] 165–75 (1938).

[14] (*a*) I. E. Sproat, C. C. Treischel, and E. W. Emrich, "Use of Organic Dispersing Agents in Casting Slips," *Bull. Amer. Ceram. Soc.*, **19** [2] 47–58 (1940).

(*b*) I. E. Sproat, C. C. Treischel, and E. W. Emrich, "All-American Sanitary-Ware Body," *Jour. Amer. Ceram. Soc.*, **24** [10] 311–17 (1941).

[15] G. H. McIntyre and J. T. Irwin, "Application of Gardner Mobilometer to Enamel-Slip Consistency Studies and Control," *ibid.*, **15** [8] 433–38 (1932).

[16] W. K. Carter and R. M. King, "Sodium Aluminate as an Electrolyte for Casting-Slip Control," *ibid.*, **15** [8] 407–409 (1932).

[17] J. T. Irwin and R. E. Bevis, "Modification of the Bingham Plastometer," *ibid.*, **21** [2] 66–68 (1938).

[18] (*a*) G. A. Loomis, "Properties of Clay Casting Slips," *ibid.*, **23** [6] 159–62 (1940).

(*b*) G. A. Loomis, "Properties of Clay Casting Slips," *Ohio State Univ. Eng. Expt. Sta. Circ.*, No. 39, 23 pp. (Jan., 1941); *Ceram. Abs.*, **20** [6] 150 (1941).

[19] G. W. Phelps, "Notes on Casting," *Bull. Amer. Ceram. Soc.*, **20** [9] 313–15 (1941).

[20] (*a*) W. H. Earhart, "Use of North Carolina Kaolin in Casting Bodies," *ibid.*, **19** [5] 163–68 (1940).

(*b*) W. H. Earhart, "Use of Washed North Carolina Kaolin as an Ingredient in Porcelain Bodies," *Ohio State Univ. Eng. Expt. Sta. Circ.*, No. 42, 40 pp. (Nov., 1941); *Ceram. Abs.*, **21** [7] 147 (1942).

[21] C. G. Harman, "Some Characteristics of Illinois Pottery Clay," *Jour. Amer. Ceram. Soc.*, **23** [1] 26–29 (1940).

[22] C. G. Harman, Laboratory Experiments, University of Illinois, First Semester, 1939–1940.

Fig. 1.—Drier for moisture compensation and confectioner's stirrer for preparation of slips.

analyses are also important, but the first-named properties were believed to have the greatest practical usefulness.

(1) Slip Preparation

In all tests on individual clays, except as noted, a mixture of 50 clay–50 flint was used. This mixture approximated the clay-to-nonplastic ratio in the average whiteware body, and the inclusion of flint expedited testing. Air-floated or pulverized clays, compensated for moisture, were used in all cases. The flint and the clay were mixed dry in a ball mill for 16 hours. All slips were prepared by means of a confectioner's stirrer (Fig. 1) similar to the soil-dispersion stirrer described in A.S.T.M. designation D 422. A clay-flint mixture (dry basis) of 350 gm. was used in all cases. The water and the desired amount of electrolytes were mixed thoroughly in the mixing cup. The dry material was added and mixing was continued for 5 minutes; 525 cc. (150%) of distilled water were used for all ball clays and 315 cc. (90%) for all kaolins and china clays. Compensation was always made for the water content of the clays and the water added in the electrolyte solutions. The electrolyte was 60% *N* brand sodium silicate, and 40% sodium carbonate, added as separate solutions (1 cc. = 0.21 gm. of *N* brand sodium silicate; 1 cc. = 0.14 gm. of soda ash).

The prepared slips were sealed in glass jars and aged at room temperature (75° to 85°F.) for 24 hours. The jars were placed in a water bath at 30°C. to insure a uniform slip-testing temperature. After not less than

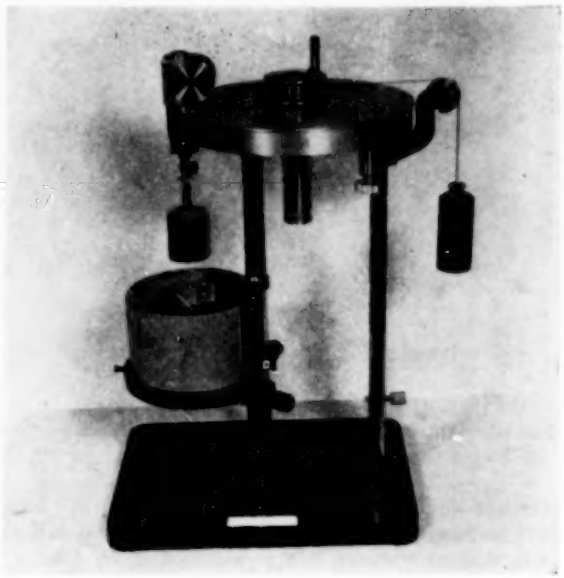

Fig. 2.—Stormer viscosimeter for thixotropy tests.

30 minutes in the water bath, the slip was stirred or remixed as required and tested.

The method of slip preparation was standardized to facilitate duplication of results. In slip testing, such factors as mixing procedure, aging, and temperature must be controlled.

(2) Fluidity

Fluidity, as a slip property, is known by various names, such as viscosity, consistency, or plasticity, depending on the type of test apparatus used. A Marriotte tube viscosimeter having a cylindrical bore of $2^1/_8$ in. in diameter with a $^1/_4$-in. orifice was chosen for the present tests; 350 cc. of slip were introduced into the tube. The time required for the last 100 cc. of 150-cc. flow was determined and assigned as the "fluidity" of the particular slip; the water standard for the viscosimeter was 21 seconds.

(3) Thixotropy

A Stormer viscosimeter (Fig. 2) was selected to determine any thixotropic tendencies. This instrument depends on the resistance to rotation under constant torque of a cylinder immersed in the slip contained in a baffled cup. The number of revolutions of the cylinder in exactly 15 seconds was used as a measure of fluidity in these tests. Tests were conducted at intervals of 0, 2, 5, and 10 minutes, thus permitting an observation of any thickening or thixotropic tendencies. A slip temperature of 30°C. was maintained during the tests.

(4) Permeability

The method used by Harman[21] was modified and used for all permeability tests. A 1000-ml. vacuum flask combined with a Büchner funnel having a perforated plate diameter of approximately 91 mm. was connected to a source of controlled vacuum supplied by

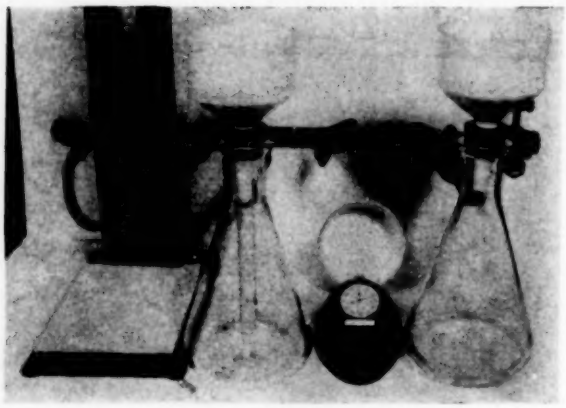

FIG. 3.—Apparatus for permeability, casting-rate, and water-retention tests.

a water aspirator or vacuum pump (Fig. 3). A negative pressure of 65 cm. of mercury as measured with an open-end manometer was maintained in all cases by adjustment with a needle valve to admit atmospheric air as required. No barometric pressure compensation was required with this constant pressure method of adjustment.

One sheet of filter paper* was placed in the funnel, and the vacuum was applied. A sufficient amount of water was then poured into the funnel to wet the paper. After the removal of all free water and with the vacuum continuously applied, a slip sample sufficient to yield exactly 10 gm. of dry material and 25 cc. of water was poured onto the wetted filter paper from a small beaker. The beaker was immediately rinsed with 25 cc. of distilled water, which was then poured into the slip in the funnel. This rinsing required approximately 5 seconds. The large excess of water caused the slip to settle out almost immediately into a firm cake resembling a layer of cast body. The surface of the slip was continuously watched, and as soon as the first evidence of the disappearance of the excess water (clearly indicated by the loss of light reflectance) from the top of the filter cake occurred, a measured amount of distilled water was poured into the funnel, and the time for its removal as indicated by the same end point was determined with a stopwatch. This was repeated until five such increments had been extracted, and a plot of time versus total water removed was made to determine the permeability. Straight-line plots were obtained in all cases, and permeability was reported as cubic centimeters per second (Fig. 4). The water of preparation extracted from the slip was neglected in the calculations, and it was assumed that the water retention was uniform throughout a given test. Five increments of 25 cc. each were used for kaolins or china clays, and five increments of 10 cc. each for ball clays (Florida kaolin was treated as a ball clay). This difference between ball and china clays was established for the sake of expediency.

* The filter paper used in the Büchner funnel was Schleicher & Schull, No. 589, White Band, 9 cm. in diameter, of medium texture and double-washed.

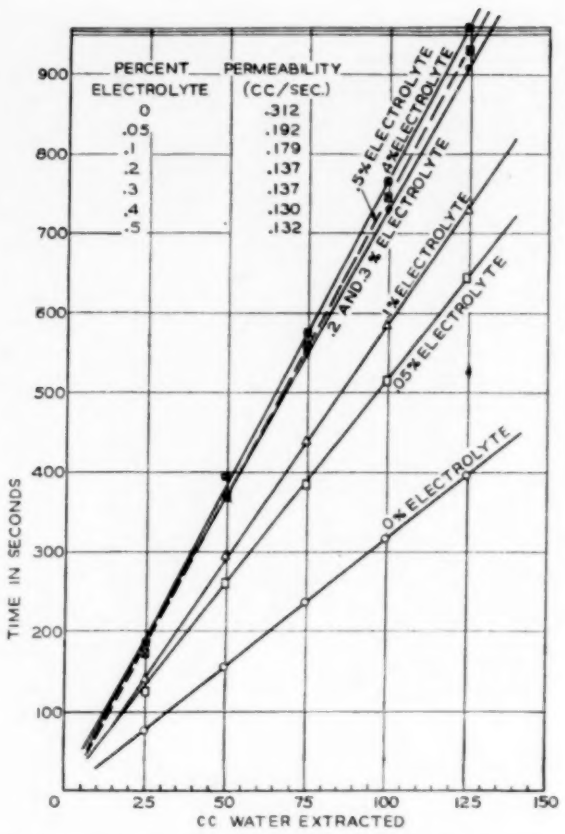

FIG. 4.—Effect of electrolyte on permeability of kaolin A.

(5) Casting Rate

The casting-rate tests were conducted using a Büchner funnel arrangement similar to that described for permeability testing in section II (4), with the addition of a 25-cc. graduate inside the vacuum flask to collect the extracted water for continual measuring and a glass plate to cover the top of the funnel to prevent excessive evaporation. In conducting these tests, a second vacuum flask was used to wet the filter paper as previously described, and the funnel was immediately transferred to the flask containing the graduate. Kaolin or china-clay slip, in the amount of 70 gm., or 40 gm. of ball-clay slip was weighed into a tared beaker. With the vacuum applied continuously, the slip was poured into the funnel and a stopwatch was used to time the rate of water removal. The beaker from which the slip was poured was weighed, and a correction was always applied to the original slip weight to determine the exact quantity actually poured into the funnel. An approximate correction (0.5 to 2.5 gm.), determined by experience, was applied in weighing out the slip in the beaker to compensate for that lost on the beaker walls. A more uniform slip weight in the funnel was thus made possible. Beakers coated with paraffin or wax were also used on occasion to prevent the adherence of the slip to the beaker walls, but this method was not entirely satisfactory owing to a tend-

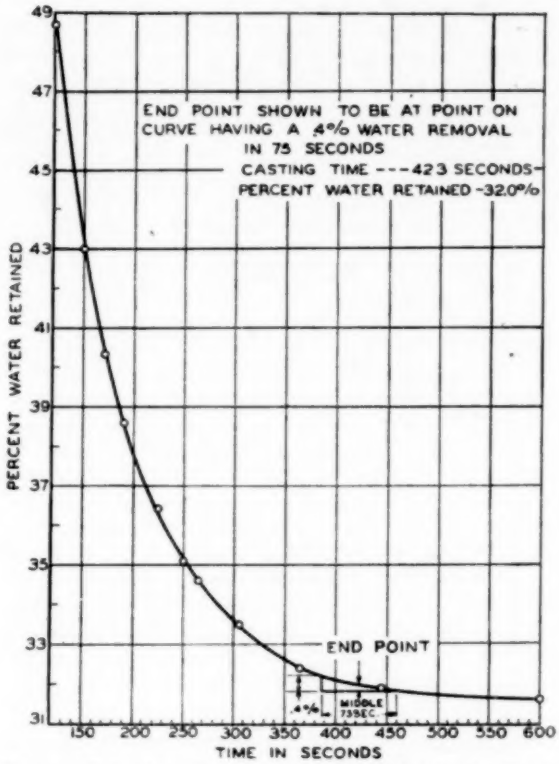

FIG. 5.—Selection of casting rate end point for kaolin A; 90% water and 0.2% electrolyte.

ency of the coated walls to become progressively ineffective with continual use.

In observing the rate of water removal, readings were taken only frequently enough to permit accurate plotting of time versus percentage of water retained. Experience is the best criterion for determining when readings should be taken because any arbitrary rule would result in an excessive or an insufficient number of readings in some cases. The frequency of reading was arbitrarily governed by the rates of water removal being observed, but two typical procedures were as follows:

(*A*) *Fast Casting Slips:* The time for 3-cc. water removal is recorded and then at every 2-cc. increment until the time interval for 2-cc. removal exceeds 2 minutes; the amount of water removed is recorded for every 2-minute increment of time until the rate of extraction is less than 0.2 cc. per 2 minutes; and the time interval for every 0.2-cc. increment is then recorded until the interval exceeds 5 minutes.

(*B*) *Slow Casting Slips:* The time for 3-cc. water removal is recorded and then at every 2-cc. increment until the time interval for the 2-cc. removal exceeds 3 minutes; the amount of water removed is recorded for every 3-minute increment of time until the rate of extraction is less than 0.2 cc. per 3 minutes; and the time interval for every 0.2-cc. increment is then recorded until the interval exceeds 5 minutes.

At the time the water extraction was terminated, that is, when the increment was less than 0.2 cc. per 5 minutes, the cast clay was removed from the funnel, separated from the filter paper, and weighed on a balance accurate to 0.05 gm. After thorough drying at 100°C., followed by cooling in a desiccator, the water which remained after casting was determined by reweighing. By simple deduction, the total amount of water actually removed in the simulative casting was then determined. In each case, the amount of water actually extracted as shown by this calculation was somewhat higher than the amount indicated by observation. A proportionate correction was then applied to each of the observed readings by a simple calculation. The application of this correction was easy to make and yielded more reliable results than the use of the uncorrected observed values. The discrepancy between the observed and corrected values was largely attributable to a variable amount of water remaining in the funnel stem and to limited evaporation inside the flask.

In the case of casting slip, both fast and slow, the casting rate for comparisons was arbitrarily selected from the plot (Fig. 5) as 0.4% of water removed (dry basis) per 75 seconds. This casting rate was assigned a cumulative time value which was indicative of the slip in question. This method of assigning casting-rate values was selected after consideration of several other reference points because it appeared to yield a comparatively true value in a minimum of testing time. The selection of this point from a typical curve in Fig. 5 shows that its position is sufficiently beyond the point of rapid change of rate as to be duplicable and reliable.

(6) Water Retention

The values for water retention were determined correlatively during the casting-rate tests, using the same data and plots. The percentage of water retention was that amount of water (dry basis) which remained in the clay mass at the time that the rate of water removal was 0.4% per 75 seconds, and at this rate of extraction the casting rate was also arbitrarily determined. This procedure meant that only a single test and the selection of a single plotted reference point were necessary to determine both the casting rate and the water retention for a given slip. For control testing, a single test that indicates these two important casting properties should often be adequate.

(7) Organic Content

A hydrogen peroxide method was used to determine the organic content. Robinson[23] compared hydrogen peroxide methods to combustion methods and reported that both are useful but are subject to errors which limit their application. It was observed that hydrogen peroxide almost completely decomposed several forms of organic matter in the presence of soil, including cellulose, humus, and lignite, but that graphite was unattacked and charcoal and coal were only partly decomposed.

[23] W. O. Robinson, "Determination of Organic Matter in Soils by Means of Hydrogen Peroxide," *Jour. Agri. Research*, **34** [4] 339–56 (1927).

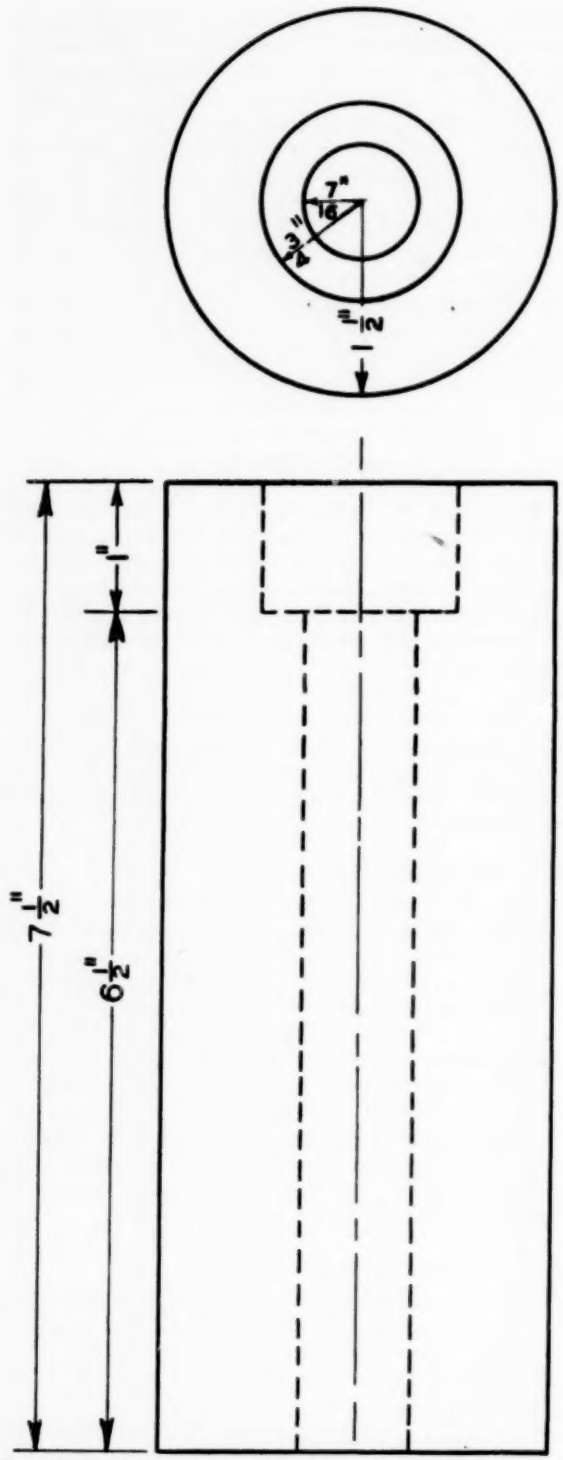

FIG. 6.—Design of plaster of Paris mold for casting experimental bars.

Tests have not been completed to determine the optimum procedure for the determination of organic content by hydrogen peroxide digestion, but a satisfactory method used in the present tests was as follows:

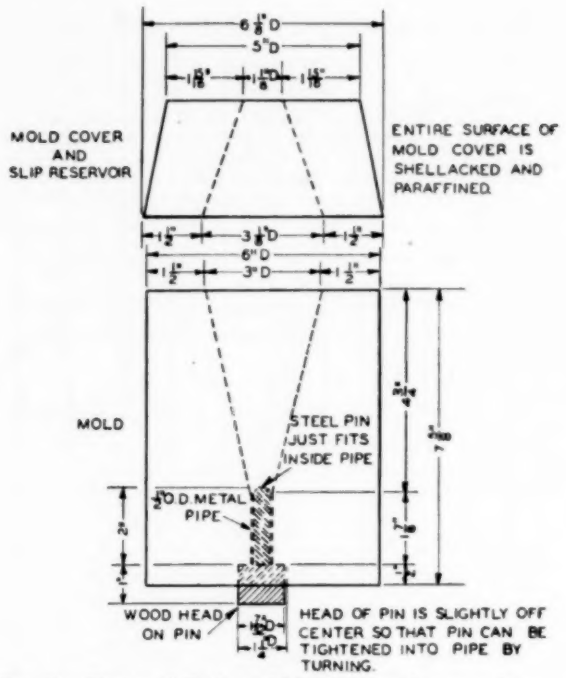
6 1/8" D
5" D
MOLD COVER AND SLIP RESERVOIR
ENTIRE SURFACE OF MOLD COVER IS SHELLACKED AND PARAFFINED.
3 1/8" D
6" D
3" D
MOLD
STEEL PIN JUST FITS INSIDE PIPE
D METAL PIPE
WOOD HEAD ON PIN
HEAD OF PIN IS SLIGHTLY OFF CENTER SO THAT PIN CAN BE TIGHTENED INTO PIPE BY TURNING.

FIG. 7.—Plaster of Paris mold for cup-casting rate determination.

Approximately 2 gm. of dry clay, preferably in powdered form, were placed in a 600-cc. tared beaker. The weight of this sample was determined to 0.001 gm., although the sample weight itself was not critical. Because of the hygroscopic nature of dry clay, it was inadvisable to attempt a direct weighing of the sample in the beaker, and a circuitous method was followed. A sample of the clay in amount larger than that to be used was placed in an unstoppered weighing bottle of known weight. After thorough drying at 110°C., the bottle was stoppered, cooled, and weighed to determine the amount of dry clay contained therein. Approximately 2 gm. of the dry clay were discharged into the 600-cc. beaker, and the bottle was immediately restoppered and weighed. The exact amount of dry clay in the beaker was then determined by deduction.

A 50-cc. sample of 10% hydrogen peroxide was mixed with the clay in the beaker, and the contents were digested on a hot plate or over a low gas flame until nearly dry (1 to 2 hours). Frequent manipulation of the beaker promoted the reactions. The beaker was then transferred to a drying oven to avoid any loss of material by spattering. An oven temperature of 150°C. was maintained to insure evaporation of organic acids (acetic, oxalic, etc.) which may have been present. The completely dried sample in the beaker was cooled in a desiccator, and its weight was determined accurately as rapidly as possible. The latter precaution was taken to reduce the time during which the clay adsorbed hygroscopic water. To minimize the error resulting from hygroscopic water, the weighed sample in the beaker was redried and reweighed. A flask which can be stoppered after drying facilitates the test and obviates the redrying procedure.

The loss in weight of the sample caused by the hydrogen peroxide digestion was assumed to be the total organic content and was calculated as percentage of weight of the original sample.

(8) Shrinkage

All bar specimens were cast in $^7/_8$-in. diameter molds of the type shown in Fig. 6. The cast collars provided a means of suspension which largely eliminated drying and firing warpage.

The underside of a collar adjacent to the bar, moreover, provided a reliable reference mark for the determination of dry or fired shrinkage, the other reference mark being the far end of the specimen. It was thus possible to determine total drying shrinkage without neglecting the shrinkage that occurred in the molds. The method as used was an improvement over the method of casting shrinkage marks directly onto bars, inasmuch as split molds were not required.

All bar specimens were cast from 50 clay–50 flint mixtures prepared into slips by the use of an electrolyte and a water content found to be appropriate for the compositions in question. Each of these slips contained decidedly less water than was used in conducting previous tests because optimum casting behavior was not associated with the low specific gravity slips used for the casting-rate and permeability tests.

(9) Transverse Strength

Cast bars, prepared as previously described, were used for all transverse strength tests. The specimen collars were removed before testing by sharp, directed raps with an appropriate tool, such as a brick hammer. Dry transverse strengths were determined on a 2-in. span and fired transverse strengths on a 5-in. span. A Tinius Olsen testing machine employing specially selected springs was used for the tests. Springs of 250-, 500-, and 1000-lb. capacity were used, depending on the strength ranges of the specimens.

(10) Cup-Casting Test

To compare the simulated casting-rate and water-retention tests with an actual casting test, a cup-casting test was devised. Plaster of Paris molds were used (Fig. 7). A dried mold was wetted by a standard procedure and then dusted with talc. The mold was filled with slip and cast for ten minutes, maintaining a uniform head. The bottom plug was then removed, the mold was allowed to drain, and the top section was removed shortly thereafter. After 40 minutes of drying with the top covered to prevent air circulation, the cast cup was trimmed at the edges, removed, and weighed. It was then dried completely at 110°C., and the weight and average thickness were determined after cooling in a desiccator.

III. Casting Test Control

It is important in conducting tests on casting clays and bodies that all variables be controlled; for example, the mixing procedure, slip temperature, and aging have a controlling effect on slip properties and casting behavior. In developing the Büchner funnel tests for the determination of casting rate, permeability, and water retention, it was desired to know the optimum standard procedures and the permissible deviation from these procedures. A series of tests was conducted, in each of which the effect of one specific known variable was determined. The effects on casting rate and water retention were observed in each case because of the primary importance of these properties in any evaluation of casting behavior. The following variable factors were studied: (1) water content (sp. gr.) of slip, (2) quantity of slip used, (3) temperature of slip, (4) aging of slip, (5) mixing time, (6) sequence of mixing, (7) vacuum pressure, (8) clay-flint ratio, (9) feldspar vs. flint as nonplastic, and (10) flint particle size.

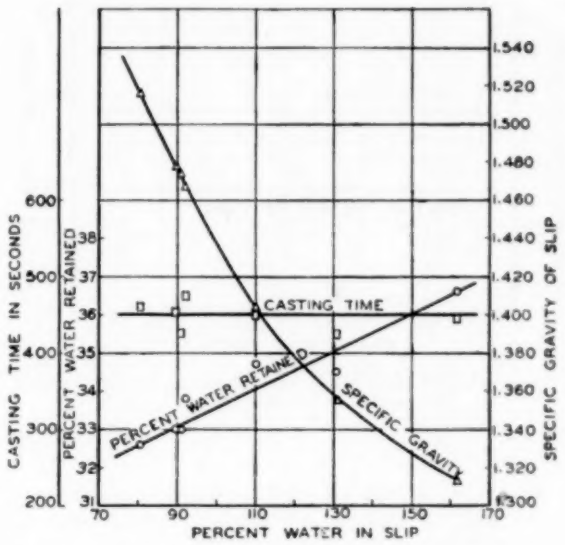

FIG. 8.—Effect of water content; kaolin A, 0.2% electrolyte.

No comparisons should be made between the values obtained in the different series of tests because of the varied procedures used in the slip preparation.

Unless otherwise noted, the water and electrolyte contents used with the four clays as tested throughout the investigation were as follows:

	Water (%)	Electrolyte (%)
Kaolin A	90	0.2
Kaolin B	90	0.2
Ball clay C	150	0.2
Ball clay D	150	0.2

(1) Water Content of Slip

Using kaolin A, slips were prepared with a range of water content from 80.8 to 161.9% and a constant electrolyte addition of 0.2% (60% sodium silicate, 40% sodium carbonate). The effect on casting rate and water retention is shown in Table I and Fig. 8. A uniform weight of clay and flint was used in each test. This wide variation in water content, that is, a specific gravity variation of 1.313 to 1.516, had no apparent effect on the casting rate. This observation does not necessarily mean that the casting rate of every clay would be unaffected by slip specific gravity, inasmuch

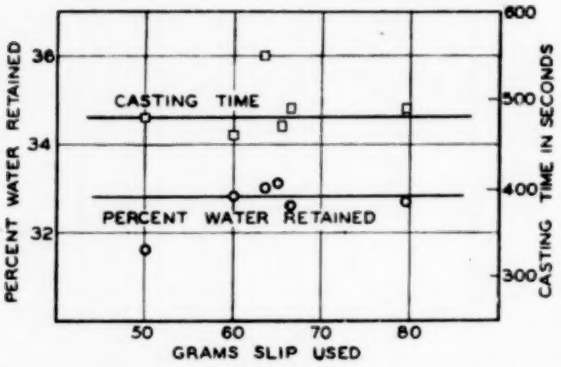

FIG. 9.—Effect of amount of slip used; kaolin A: 90% water, 0.2% electrolyte.

TABLE I

EFFECT OF WATER CONTENT OF SLIP ON KAOLIN A

Water content (%)	Specific gravity (gm./cc.)	Casting time (sec.)	Water retained (%)
80.8	1.516	460	32.6
89.7	1.477	455	33.0
91.0	1.474	425	33.0
92.0	1.467	475	33.8
110.0	1.404	450	34.7
130.9	1.356	425	34.5
161.9	1.313	445	36.6

as a slow-casting kaolin or ball clay possibly would not show the stability of casting rate noted for kaolin A.

The amount of water retained in the casts of kaolin A increased in proportion to the water content of the slip, that is, in inverse proportion to the specific gravity of the slip. The maximum difference in the water retained was 4%, indicating that the water content of the slip must be controlled but that a variation of up to 20% in water content could be tolerated. The standards adopted were 90% water for kaolins and china clays and 150% water for ball clays (dry basis).

(2) Quantity of Slip Used

Kaolin A was used in these tests, during which the quantity of slip was varied from 50 to 80 gm. The effects on casting rate and water retention are shown in Table II and Fig. 9. No effect of slip quantity on casting rate was observed, and the amount of water retained was unaffected except for a moderate reduction below 60 gm. A 70-gm. quantity of kaolin slip was therefore adopted as standard. Although there were indications that the amount of slip need not necessarily be closely standardized, accurate control was required to avoid errors in calculation.

For testing ball clays, a 40-gm. quantity of slip was adopted as the standard although the extent of its effect was not determined for ball clay.

(3) Slip Temperature

Tests were conducted on kaolin A in which the slip temperature was varied from 15° to 39°C. (59° to 102°F.), a range which would include all probable variations in room temperature in a laboratory. The results are shown in Table III and Fig. 10. There was a moderate tendency for increase in casting rate with increase in temperature, although the maximum difference noted was only 85 seconds. The amount of water retained was not affected by slip temperature except for a tendency toward an increase above 35°C. In view of these results, a slip-testing temperature of 30°C. was adopted as standard, and this represents a temperature which can be attained in most cases by the use of a simple constant-temperature bath.

(4) Aging of Slip

Both kaolin A and ball clay D were used in the aging tests, which included the determination of casting properties of slips after aging for 1 and 4 hours and 1, 2, 7, and 14 days. The results are shown in Table IV and Figs. 11 and 12. The graphs were plotted on semi-log paper so that the shorter aging periods of a few hours could be shown for comparison with longer periods of one or two weeks.

For kaolin A, the casting time was unchanged by aging for one day but showed a moderate increase in aging an additional day. The slip remained essentially stable thereafter when aged as much as twelve more days. The water-retention values decreased progressively a moderate amount during the first day, increased somewhat during the second day, and remained essentially stable during the remaining twelve-day aging period. The maximum differences of 95 seconds in casting time and 1.3% in water retained were relatively low, indicating that aging of kaolin A had no major effects.

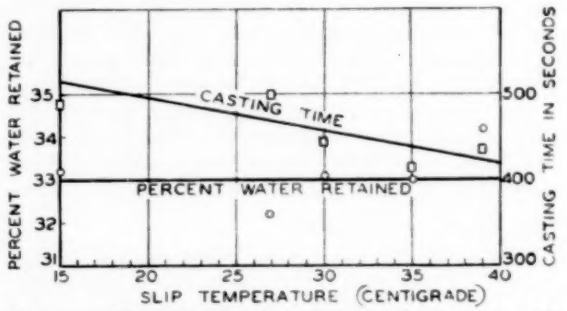

FIG. 10.—Effect of slip temperature; kaolin A: 90% water, 0.2% electrolyte.

TABLE II

EFFECT OF AMOUNT OF SLIP USED ON KAOLIN A

Slip used (gm.)	Casting time (sec.)	Water retained (%)
50.2	480	31.6
60.0	460	32.8
68.6	480	33.0
70.1	550	33.1
71.5	470	32.6
79.5	490	32.7

TABLE III

EFFECT OF TEMPERATURE ON KAOLIN A

Slip temp. (°C.)	Casting time (sec.)	Water retained (%)
15	490	33.2
27	500	32.2
30	445	33.1
35	415	33.0
39	435	33.2

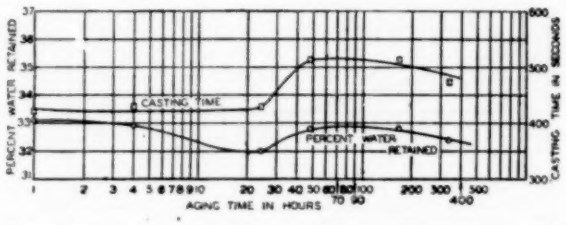

Fig. 11.—Effect of aging on kaolin A, semilog plot; 90% water, 0.2% electrolyte.

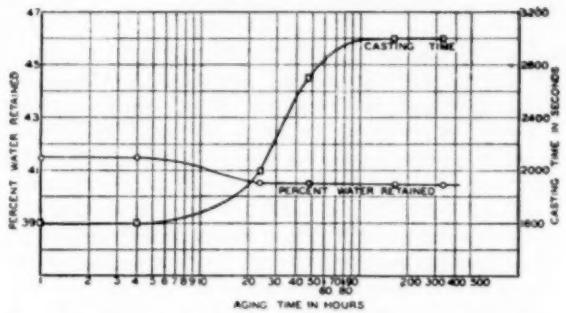

Fig. 12.—Effect of aging on ball clay D, semilog plot; 150% water, 0.2% electrolyte.

Table IV
Effect of Aging Time

Age	Casting time (sec.)	Water retained (%)
	Kaolin A	
1 hr.	420	33.1
4 hr.	430	32.9
1 day	430	32.0
2 days	515	32.8
1 week	515	32.8
2 weeks	475	32.4
	Ball clay D	
1 hr.	1600	41.5
4 hr.	1600	41.5
1 day	2000	40.5
2 days	2700	40.5
1 week	3000	40.5
2 weeks	3000	40.5

With ball clay D, the values for water retention were stable for the first few hours and then dropped off 1% to become stable again after one day of aging. The casting time of ball clay D was stable during the first four hours of aging, following which it increased gradually and did not become restabilized until a week had passed. The variation of 1400 seconds in the ball-clay casting time as opposed to only 100 seconds for the kaolin was undoubtedly due in part to the greater amount of organic matter in the ball clay.

A 24-hour aging period was adopted as the standard for casting tests as a matter of expediency inasmuch as it was believed that most clays would have characteristic aging behaviors.

(5) Mixing Procedure

(*A*) *Mixing Time:* The effect of variations in mixing time of 2 to 30 minutes was determined for slips of kaolin A and ball clay D. Table V and Figs. 13 and 14 show the results of these tests, all slips being aged one day before testing. With both clays, the casting time increased with progressive increases in mixing time. Comparing the two extreme mixing times of 2 and 30 minutes, the casting time increased from 360 to 820 seconds for kaolin A and from 890 to 2300 seconds for ball clay D. The water retained in the casts for kaolin A progressively decreased from 33.9 to 29.5% with increase of mixing time up to 30 minutes. For ball clay D, a progressive decrease from 42.8 to 40.3% was obtained by an increase of mixing time up to 10 minutes, beyond which no further reduction occurred.

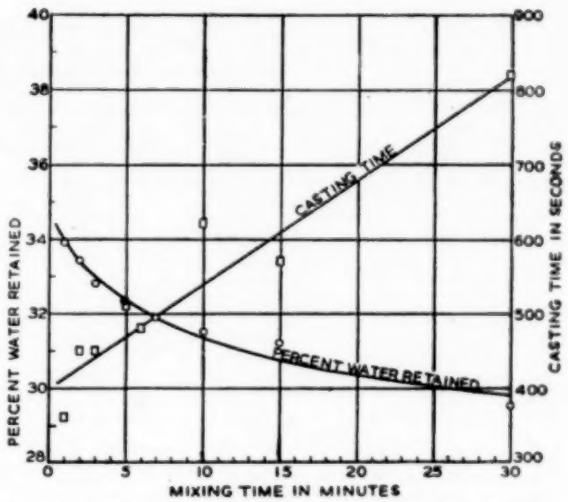

Fig. 13.—Effect of mixing time on kaolin A; 90% water, 0.2% electrolyte.

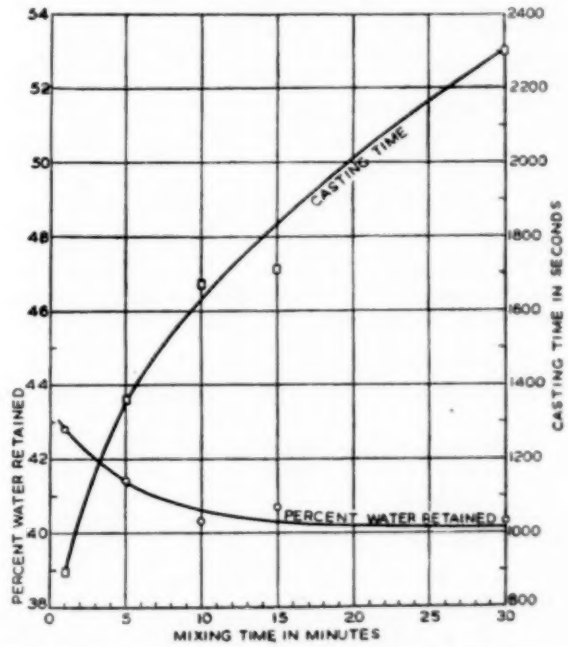

Fig. 14.—Effect of mixing time on ball clay D; 150% water, 0.1% electrolyte.

TABLE V

EFFECT OF MIXING TIME

Mixing time (min.)	Casting time (sec.)	Water retained (%)
Kaolin A		
1	360	33.9
2	450	33.4
3	450	32.8
5	510	32.3
7	480	31.9
10	620	31.5
15	570	31.2
30	820	29.5
Ball clay D		
1	890	42.8
5	1360	41.4
10	1670	40.3
15	1710	40.7
30	2300	40.3
Mixed 5 min., aged 16 hr., remixed 5 min.	1610	38.5
Mixed 5 min., aged 16 hr., remixed 30 min.	1780	38.0
Ball milled 16 hr., mixed 5 min. in mixer	1610	37.6
Ball milled 16 hr., mixed 30 min. in mixer	2600	35.4

TABLE VI

EFFECT OF SEQUENCE OF MIXING ON BALL CLAY C

Order of additions*	Casting time (sec.)	Water retained (%)
H–N–B–MS (2 min.)–S–MF (4 min.)	840	34.6
H–S–B–MS (2 min.)–N–MF (4 min.)	775	33.8
H–B–MS (2 min.)–S–N–MF (4 min.)	900	33.8
H–S–N–B–MF (5 min.)	910	32.7

* H = water, N = Na_2CO_3, B = body, MS = mixed slow, S = sodium silicate, and MF = mixed fast.

TABLE VII

EFFECT OF VARIATION OF VACUUM PRESSURE ON KAOLIN A

Vacuum pressure of Hg (cm.)	Casting time (sec.)	Water retained (%)
55	435	33.9
60	385	33.6
65	435	31.8
70	440	32.8
73	390	31.7

The effects of ball-mill preparation versus dispersion with the confectioner's stirrer were observed for ball clay D (Table V) in an attempt to devise a mixing procedure which would give maximum dispersion and thus a truer result. Neither mixing with the stirrer nor ball milling gave indications of producing a slip which was in a stable condition with respect to additional mixing because remixing for periods of 5 and 30 minutes following aging yielded variable results in both cases. The greatest effect of remixing was noted for the ball-milled slip, which exhibited a greatly increased casting time for the 30-minute remixing time. With a 5-minute remixing period, similar results were obtained by the ball-milling and stirring methods of preparation.

In view of the limited number of tests conducted, it was not possible to determine the causes for the failure to produce clay slips which were stabilized with respect to mixing, although such factors as degree of dispersion, progressive base exchange, and bacterial action were probably involved. It was quite apparent, however, that casting behavior is materially affected by mixing time and intensity, whether laboratory testing or production usage is being considered.

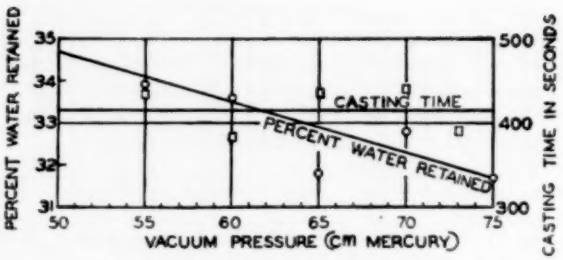

FIG. 15.—Effect of vacuum pressure variations, kaolin A; 90% water, 0.2% electrolyte.

(*B*) *Sequence of Mixing:* A limited number of tests was conducted to determine whether or not apparent differences would result from variations in the sequence of mixing together the water, electrolyte solutions, and the clay-flint body mixture. The results obtained for ball clay C are given in Table VI. Maximum differences of 1.9% for the water retained and 135 seconds for the casting time were noted. Although these differences are not of high magnitude, they indicate the desirability of using a standard sequence in the preparation of casting slips for test as well as in production usage. The tests were insufficient in number to justify any conclusions as to optimum procedures, but the standard order of mixing adhered to throughout the other phases of this investigation was as follows: Water and electrolytes mixed for 1 minute, clay-flint mixture added, and mixing continued for exactly 5 additional minutes. Following a 24-hour aging period, the slip was remixed for 15 seconds prior to testing.

(6) Vacuum Pressure

Using kaolin A, the vacuum pressure applied to the slip during testing was varied from 550 to 730 mm. (21.7 to 28.7 in.) of mercury as measured with an open-end manometer. The effects on casting properties are shown in Table VII and Fig. 15. The pressure variation had no apparent effect on casting rate, but the amount of water retained tended to decrease with increase in pressure. A maximum difference of 2.2% of water retained was noted. A pressure of 650 mm. of mercury was finally adopted as standard because this degree of vacuum can readily be maintained either with a vacuum pump or a water aspirator.

(7) Clay-to-Flint Ratio

To determine the effects produced by variations in the clay-to-flint ratio, a series of tests was conducted in which the ratio was varied from 40–60 to 60–40. The results for kaolin A are shown in Table VIII. It was indicated that the clay-to-flint ratio in the range studied had no effect on casting rate. A maximum variation of 3.6% was noted in the amount of water retained, and the values showed a tendency to increase in

TABLE VIII

EFFECT OF CLAY–FLINT RATIO ON KAOLIN A

Clay (%)	Flint (%)	Casting time (sec.)	Water retained (%)
60	40	490	33.5
52.5	47.5	490	33.3
50	50	510	31.8
47.5	52.5	470	32.4
40	60	490	29.9

TABLE IX

EFFECT OF SUBSTITUTION OF FELDSPAR FOR FLINT

Feldspar (%)	Flint (%)	Casting time (sec.)	Water retained (%)
	50% kaolin A		
0	50	445	32.5
10	40	470	33.1
20	30	425	33.0
30	20	445	33.1
40	10	435	33.7
50	0	460	34.0
	50% ball clay D		
0	50	2030	39.8
10	40	2170	40.1
20	30	2310	40.2
40	10	2350	39.1
50	0	2330	39.1

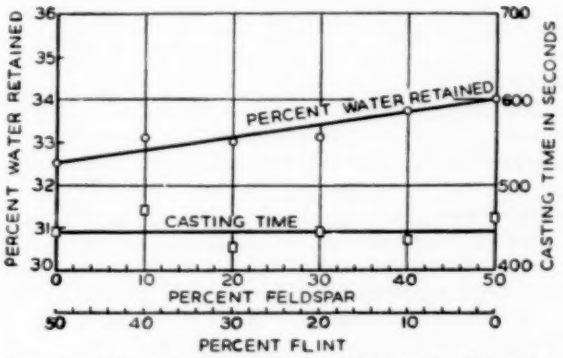

FIG. 16.—Effect of substitution of feldspar for flint using kaolin A; 90% water, 0.2% electrolyte.

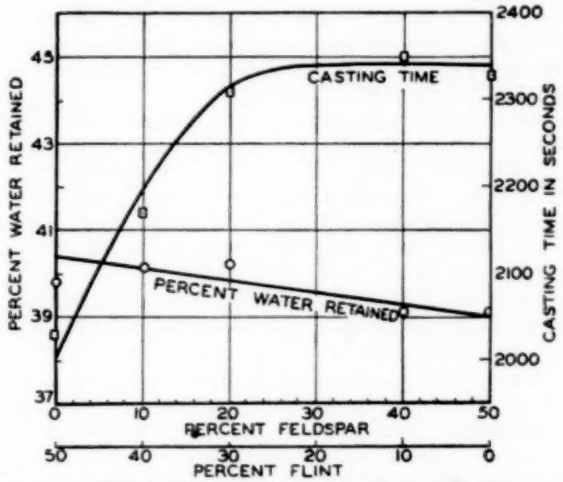

FIG. 17.—Effect of substitution of feldspar for flint using ball clay D; 150% water, 0.2% electrolyte.

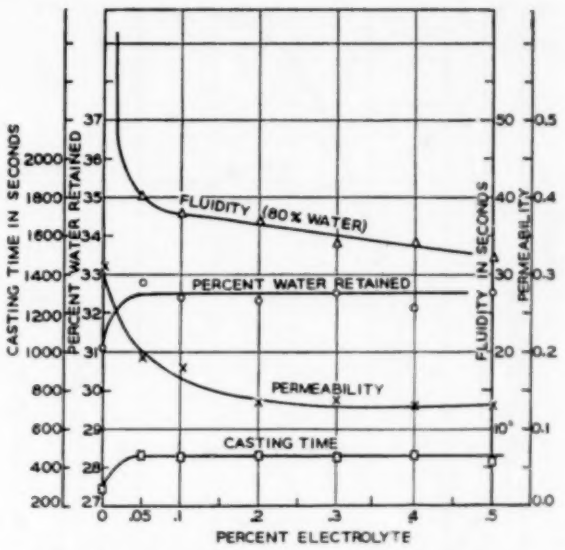

FIG. 18.—Effect of electrolyte content on kaolin A; 90% water.

proportion to the clay content, that is, to increase with the clay-to-flint ratio. The standard adopted for testing was a clay-to-flint ratio of 50–50 because this amount represents the ratio of clay to nonplastics in the average whiteware body.

(8) Feldspar vs. Flint as Nonplastic

Because feldspar as well as flint is a common constituent in whiteware bodies and because there is reason to believe that the solubility and the grain size of feldspar as compared to flint affect casting behavior, a series of tests was conducted in which a feldspar progressively replaced the flint in 0 to 100% amounts. Kaolin A and ball clay D were tested (see Table IX and Figs. 16 and 17).

With kaolin A, the substitution of feldspar for flint caused a moderate, progressive increase in the water retained, but the maximum increase for total replacement was only 1.5%. The casting time for kaolin A was unaffected by feldspar substitution; this result was consistent with the wide working range of this clay with respect to electrolyte (Fig. 18). The substitution of feldspar for flint with ball clay D caused the percentage of water retained to decrease and the casting time to increase. The resulting curves were quite similar to the curves obtained from the addition of increments of of electrolytes to this clay (Fig. 19). The solubility of feldspar is thus shown to have a marked effect on the properties of casting slip. The slight variations between the feldspar curve and the electrolyte curve may be due to the difference in particle size between the feldspar and the flint and/or to the fact that the electrolyte produced by the solution of feldspar may affect the clay differently than the silicate-carbonate electrolyte.

A standard nonplastic, therefore, apparently should be used for all comparative tests, particularly when the clays exhibit varying casting properties as determined by the amount of electrolyte present. The effect of

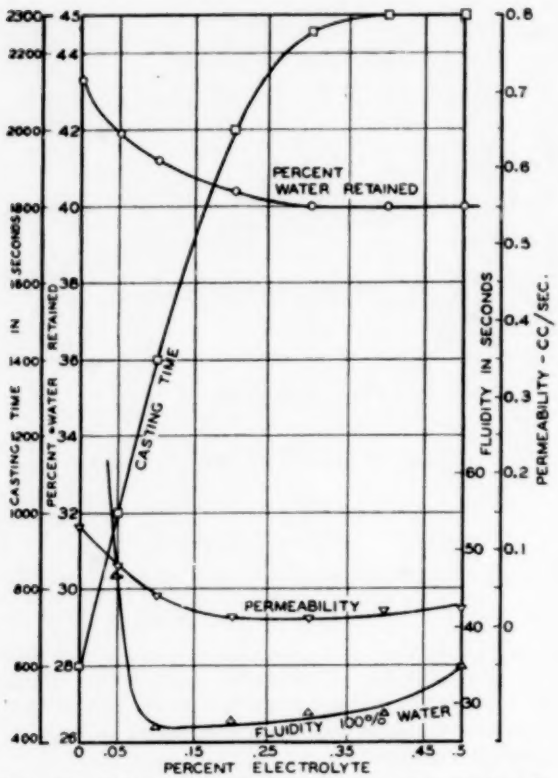

FIG. 19.—Effect of electrolyte content on ball clay D; 150% water.

feldspar solubility, moreover, must be considered in the adjustment of casting slip inasmuch as the alkali present in solution from this source may exert an important effect.

(9) Flint Particle Size

Using ball clay D, the effect of varying the flint particle size was observed (Table X and Fig. 20). Three flints were used, differing only in particle size, that is, in specific surface as determined by the Andreasen pipette method. As the specific surface of the flint increased from 1740 to 3840 sq. cm. per gm., the amount of water retained progressively decreased from 41.0 to 38.9% and the casting time from 2100 to 1800 seconds. This decrease might be explained by the fact that the increased number of flint particles present tended to separate the clay particles more effectively and thus exerted an increasing effect on casting properties. The effective amount of flint provided by the finer materials, moreover, may possibly have caused the 50 clay–50 flint mixtures to behave in a manner comparable to mixtures of decidedly higher flint content based on weight amounts. Thus, whereas the surface area of the clay remained constant, the 222% increase in specific surface of the flint from the coarsest to finest material tended to produce an effect comparable to providing a 31 clay–69 flint mixture by weight comparison. Such a marked deviation would not be desirable despite the evidence previously cited that considerable variations in clay-to-flint weight ratios may be tolerated.

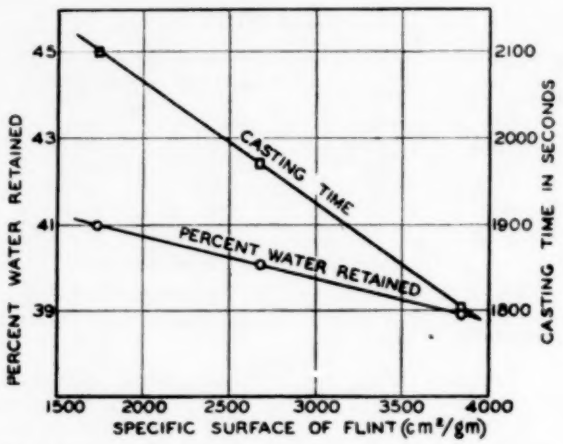

FIG. 20.—Effect of particle size of flint on ball clay D 150% water, 0.2% electrolyte.

TABLE X

EFFECT OF PARTICLE-SIZE VARIATION OF FLINT ON BALL CLAY D

Flint specific surface (cm.²/gm.)	Casting time (sec.)	Water retained (%)
1740	2100	41.0
2680	1970	40.1
3840	1800	38.9

For all standardized testing of materials, it is proposed that a flint of controlled and constant particle size be employed, and this recommendation can readily be followed by storing a standard flint for use in casting tests.

Although no tests were conducted to determine the effect of feldspar fineness, it is logical to assume that even more pronounced effects would be observed than in the case of flint because solubility effects as well as specific surface effects would be involved.

IV. Tests on Representative Clays

Four clays were tested to determine the usefulness of the methods of test for the comparison and control of different clays as follows: (1) kaolin A (fast casting), (2) kaolin B (slow casting), (3) ball clay C (fast casting), and (4) ball clay D (slow casting).

Each clay was investigated with respect to varying quantities of electrolyte and its effect on the fluidity, permeability, casting-rate, and water-retention characteristics. The following increments of electrolyte (60 *N* brand sodium silicate and 40 sodium carbonate) were added: 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50% (dry weight basis).

Thixotropy, dry shrinkage, dry transverse strength, and organic content were also determined for each clay. The properties of all clays are given in Table XI.

In the following discussion of the effect of electrolyte, all additions refer to the weight of the clay-flint mixtures used. Thus 0.2% of electrolyte added to a slip of kaolin A, actually means 0.2% of the weight of the clay-flint mixture; in terms of the actual clay present, the amounts of electrolyte would be doubled.

TABLE XI

PROPERTIES OF INDIVIDUAL CLAYS

Electrolyte (%)	Büchner funnel tests: Fluidity (sec./100 cc.)	Permeability (cc./sec.)	Casting time (sec.)	Water retained (%)	Cup casting test: Water retained (%)	Dry weight of cast (gm.)	Dry thickness of cast (in.)	Thixotropy (rev./15 sec.): 0 min.	2 min.	7 min.	17 min.	Dry strength (lb./in.²)	Organic content (%)	Shrinkage (%): Drying	Firing (cone 12)	Total	Fired strength at cone 12 (lb./in.)²	Water Absorption (%)
								Kaolin A										
0.0		0.312	290	31.1									0.23					
.05	40	.192	460	32.8														
.1	38	.179	450	32.4														
.2	37	.137	460	32.3	30.0	255.0	0.550	11¼	7¾	6½	6¼	43		2.59	5.70	8.29	2860	19.1
.3	34	.137	450	32.5														
.4	34	.130	460	32.1														
.5	32	.132	440	32.5														
								Kaolin B										
.0		.084	900	27.5									0.0					
.05		.042	1370	28.0														
.1	37	.046	1520	27.8														
.2	38	.031	1920	30.6	29.5	92.1	.161	10	8¾	5¾	½	394		5.32	1.78	7.10	1960	20.7
.3	36	.017	2920	33.2														
.4	34	.014	3850	36.5														
.5	35	.010	4300	37.5														
								Ball clay C										
0		.533	380	33.1									1.87					
.05		.421	520	33.4														
1	42	.267	650	31.1														
2	33	.308	920	32.4	28.5	138.2	.218	11	4½	1¾	¾	271		4.00	1.50	5.30	2790	19.5
3	31	.057	1190	34.6														
.4	28	.052	1470	34.6														
.5	30	.038	1740	34.6														
								Ball clay D										
.0		.125	600	43.3									5.07					
.05	47	.080	1000	41.9														
1	27	.041	1400	41.2														
2	28	.014	2000	40.4	30.9	78.7	.146	11¾	8½	1¼	½	477		5.58	2.54	8.12	2630	18.3
3	29	.013	2260	40.0														
4	29	.024	2300	40.0														
.5	35	.025	2300	40.0														

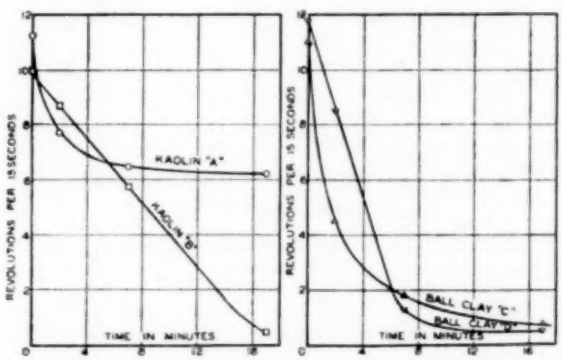

FIG. 21.—Thixotropy as determined by the Stormer viscosimeter; 0.2% electrolyte for all clays; kaolin A, kaolin B, and ball clay D, each 50% water; ball clay C, 55% water.

No comparisons were made between the casting-time values for ball clays versus kaolins because of the discrepancy in the water content of the slips employed to expedite the testing. Ball clays and kaolins were considered as two different classes of materials. Florida kaolin, however, is an exception, and it was tested as a ball clay owing to its similarity in properties. The results for this clay are not included in this report.

(1) Kaolin A

Kaolin A possessed extremely stable casting properties for a wide range of electrolyte content (Fig. 18). Only 0.1% of electrolyte was required for the development of optimum casting properties, although an addition of as much as 0.5% apparently had no undesirable effects. The extreme stability with respect to electrolyte concentration was rather unusual, and this, together with a low value of water retention and a very fast casting rate (low casting time), indicated outstanding promise for the use of kaolin A in casting bodies.

Kaolin A had a 0.2% organic content, which probably is of no consequence except that it is unusual to find organic constituents in a clay of this type. The low dry strength of 43 lb. per sq. in. was the poorest property noted for this clay and indicated the desirability of using it in combination with higher strength kaolins or appreciable quantities of ball clay. Although some thixotropy was observed (Fig. 21), the tendency was much less pronounced than with any of the other three clays tested, and it would generally be classified as nonthixotropic.

(2) Kaolin B

The differences between kaolin B and kaolin A are oustanding (Fig. 22). In fluidity and permeability characteristics, kaolin B had a wide range of electrolyte usage, with the optimum amount at 0.1 to 0.2%. The values of casting time and water retention, however, increased markedly with each successive increment of electrolyte, indicating extreme difficulty in an adjustment to obtain uniform properties. At a value of 0.2% of electrolyte, the water-retention value was comparable to kaolin A but the casting time was more than four times as high. The permeability of kaolin B was also much lower.

Kaolin B had no organic content whatever, but was distinctly thixotropic (Fig. 21). Its most outstanding

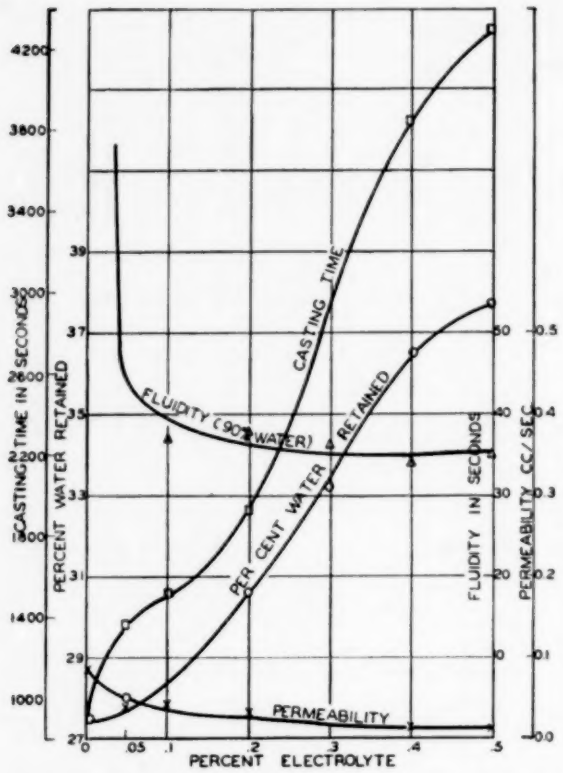

FIG. 22.—Effect of electrolyte content on kaolin B; 90% water.

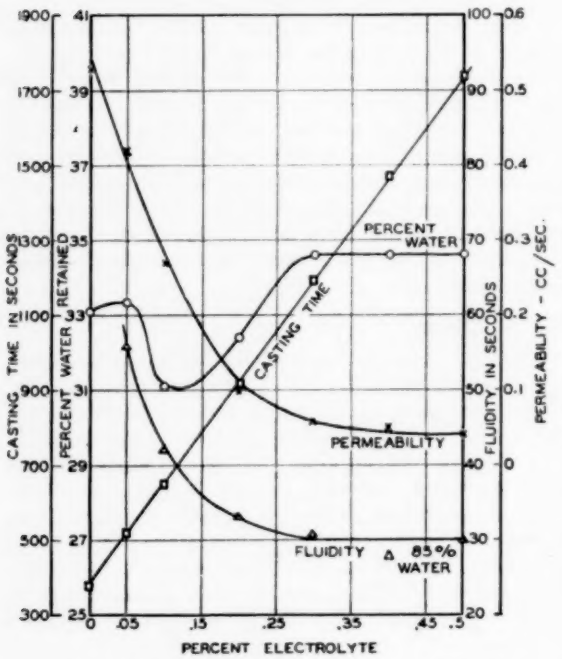

FIG. 23.—Effect of electrolyte content on ball clay C; 150% water.

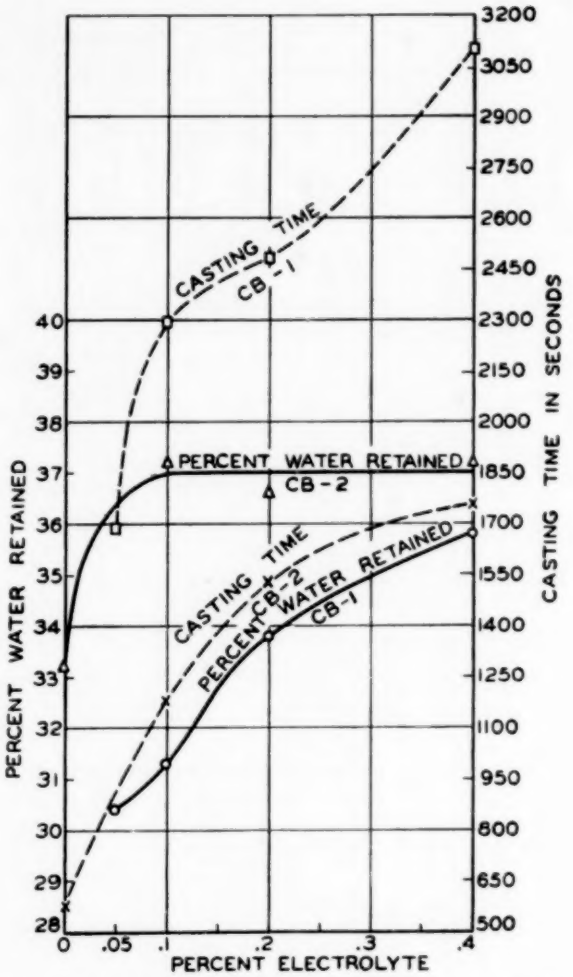

FIG. 24.—Casting properties of bodies CB-1 and CB-2; 115% water.

property of merit was its high, dry strength of 394 lb. per sq. in.

Considering the unstable casting properties with respect to electrolyte, together with the extremely slow casting rate and thixotropic character, kaolin B appeared to be an unsatisfactory casting clay.

It is interesting to observe that very slow drying qualities resulted from the use of this clay in glazes. The primary plant use, moreover, has been in plastic and dry-press bodies, with little or no application in commercial casting bodies.

(3) Ball Clay C

The fluidity and permeability data given in Fig. 23 indicate that stability was being approached with 0.2% of electrolyte, with no major change from an increase up to 0.5%. The values for water retention were about the same at 0 and 0.05% of electrolyte, but dropped off 2% at 0.1%. The values rose again and became stable at 0.3%. The 34.5% water retained in the stable range would be considered fairly low for a ball clay. Casting

TABLE XII

PROPERTIES OF BODIES

Feldspar (%)	Flint (%)	Kaolin (%) A	Kaolin (%) B	Ball clay (%) C	Ball clay (%) D	Water (%)	Electrolyte (%)	Büchner funnel test: Casting time (sec.)	Büchner funnel test: Water retained (%)	Cup casting test: Water retained (%)	Cup casting test: Dry wt. of cast (gm.)	Cup casting test: Dry thickness of cast (in.)
							Body CB–1					
30	20	15	15	10	10	115	0.05	1690	30.4			
							.1	2300	31.3			
							.2	2480	33.8			
							.4	3100	35.8			
							Body CB–2					
30	20	30	0	10	10	115	0	580	33.2			
							0.05	780	32.7			
							.1	1180	37.2	25.9	143.0	0.214
							.2	1530	36.6	26.1	108.0	.168
							.3			25.6	93.7	.142
							.4	1760	37.2	26.0	95.9	.157

time increased progressively with each addition of electrolyte, indicating that this property would be rather difficult to control. The casting-time values were lower than for most ball clays, but there was a continuous increase from 380 seconds at 0.0% of electrolyte to 1740 seconds at 0.5% of electrolyte. The permeability of ball clay C was decidedly lower than that observed for kaolin A. Kaolin B, however, had a lower permeability than either kaolin A or ball clay C.

Ball clay C contained only 1.9% organic but was decidedly thixotropic (Fig. 21). The dry strength of 271 lb. per sq. in. was not particularly high but was quite satisfactory for a fast casting ball clay.

Because of its thixotropic character and unstable casting time as affected by electrolyte and its thixotropic character, ball clay C would not be a very suitable casting clay. Its properties were somewhat intermediate between kaolins A and B.

(4) Ball Clay D

A consideration of the casting results (Fig. 19) indicated that about 0.3% of electrolyte was the optimum for this clay. Both fluidity and permeability were essentially stable in the range of 0.1 to 0.4%. The percentage of water retained became stabilized at 0.2% of electrolyte, but the water-retention values for ball clay D were distinctly higher than for the other three clays.

The casting time increased rapidly with each successive increment of electrolyte up to 0.3%. In stability of casting time and percentage of water retention, ball clay D was superior to ball clay C. The permeability of ball clay D, however, was lower than that of ball clay C.

The organic content of ball clay D was 5.1%, indicating that its excessive use might cause black coring. The most desirable property was a high dry strength of 477 lb. per sq. in. Definite thixotropic tendencies were noted.

In comparing ball clays C and D, the latter would appear to be the superior casting clay although it has higher water retention and lower permeability. The relative stability of all its properties coupled with high dry strength would justify its use in casting bodies.

V. Tests on Casting Bodies

Tests were conducted, using variable amounts of electrolyte in two casting bodies compounded from the clays previously tested, to obtain preliminary indications of the virtue of the test methods in the design of body compositions. The body compositions and test results are given in Table XII. Feldspar provided a portion of the nonplastic with flint in amounts comparable to high-tension electrical porcelain usage. The amount of water used in the slips was apportioned on the same basis as in the clay tests, namely, 90% for kaolins and 150% for ball clays.

Body CB–2 differed from body CB–1 only in the substitution of 15% of fast-casting kaolin A for slow-casting kaolin B. The results of this substitution are clearly shown in Fig. 24. This replacement of kaolin B by kaolin A resulted in a marked reduction in casting time for every electrolyte addition. The stabilizing effect of kaolin A toward variations in electrolyte, moreover, was indicated by the lower slope of the casting time curve for CB–2. The substitution of kaolin A resulted in an increase in the percentage of water retained for all increments of electrolyte used.

Although the comparative bodies tested did exhibit relative casting properties as expected, the actual results varied considerably from the values calculated on the basis of the individual clay tests (Table XI). All of the casting-time values observed were decidedly higher than the calculated values, whereas no such definite trend occurred for the water-retention values; none of these, however, deviated more than 2.8% from the calculated value.

Several factors may have contributed to the differences between the actual and calculated values. The inclusion of feldspar in the body compositions was undoubtedly an important factor. The blending of clays, moreover, does not give a straight-line variation in properties for several reasons, such as mutual base exchange, differential stability toward the effects of electrolyte, and variable density of casts as controlled by the relative degree of fineness of the clays involved. In explaining this latter assumption, consideration

need only be given to the studies of particle packing in an investigation relating to refractories.[24]

Although the clays used in bodies may not always produce an effect on casting commensurate with the amount used, it is undoubtedly true that each clay will exhibit an effect determined by its particular properties as compared with any other clay for which it may be substituted or which it may partially replace. This phase of the present investigation certainly needs considerably greater attention in order to permit the more intelligent use of data obtained for individual clays. Despite the discrepancies noted, definite promise for the study of casting bodies and the objective design of bodies is indicated by the limited number of tests herein reported.

VI. Cup Method for Casting-Rate Determination

To determine whether any correlation exists between the Büchner funnel method described here and actual casting tests, cup casting-rate tests were conducted for body CB–2 over a range of electrolyte content and for the four clays individually, using 0.2% of electrolyte (Tables XI and XII).

For most of the clays and the body, there was a decided discrepancy between the water-retention values obtained by the two methods. Thus, no outstanding differences between the four clays were apparent in the cup tests, but notable discrepancies occurred in the Büchner funnel tests, indicating a greater sensitivity in the latter test. The casting-rate criteria (wet weight, dry weight, or dry thickness) indicated that the relative casting rates in decreasing order were kaolin A, ball clay C, kaolin B, and ball clay D. Kaolin A was observed to have an extremely high casting rate compared to kaolin B, and ball clay C was considerably faster than ball clay D. These results compare favorably with the Büchner funnel test results.

The effect of electrolyte on the casting rate of body CB–2 was observed (Table XII) to be similar to that noted for the Büchner funnel tests. The comparison between the casting rates obtained with the cup tests and the casting times with the Büchner funnel test are shown in Fig. 25. The ordinate scales were selected to allow the two curves to have approximately the same general shape for comparative purposes. In the cup tests, the casting rate as determined by dry weights appeared to be more stabilized in the range of 0.3 to 0.4% of electrolyte than had been observed in the funnel tests. Using dry thickness as the criterion, however, a maximum was reached at 0.3%. No such maximum or stabilization was apparent from the Büchner funnel tests, which were consistent with the expected result.

The results of these tests indicate usefulness for the cup casting-rate test developed, but they show it to be considerably less sensitive in general than a Büchner funnel test. Production-control experience with cup casting-rate tests or their equivalent, moreover, has not always proved satisfactory. A cup casting test for comparing clays and for body slip control may be

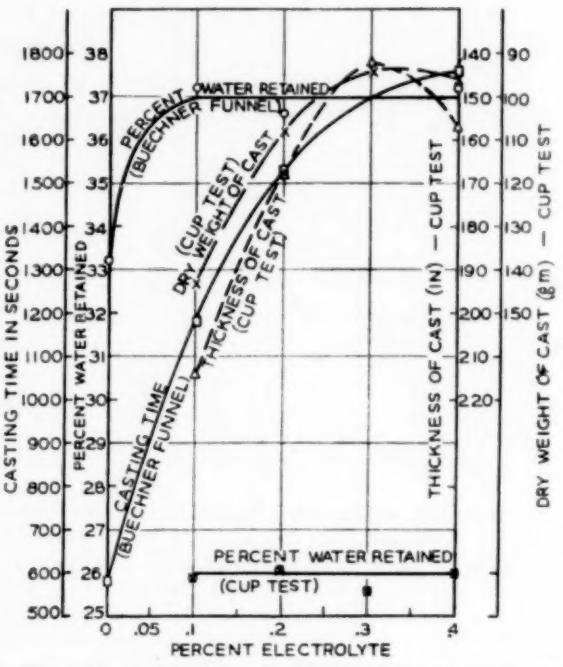
CASTING TIME IN SECONDS
PERCENT WATER RETAINED
THICKNESS OF CAST (IN) — CUP TEST
DRY WEIGHT OF CAST (gm) — CUP TEST
PERCENT ELECTROLYTE
PERCENT WATER RETAINED (BUCHNER FUNNEL)
CASTING TIME (BUCHNER FUNNEL)
DRY WEIGHT OF CAST (CUP TEST)
THICKNESS OF CAST (CUP TEST)
PERCENT WATER RETAINED (CUP TEST)

FIG. 25.—Comparison of Büchner funnel and cup casting tests on body CB–2; Büchner funnel, 115% water; cup test 50% water.

useful, but the methods herein developed for the Büchner funnel are a definite improvement because of increased sensitivity and flexibility.

VII. Summary

The tests described herein, when conducted under properly controlled conditions, appear to be satisfactory for the evaluation of casting properties and should be useful for the comparison of different clays and bodies and also for manufacturing control of individual clays and body slips. A means is provided for the study of the effect of various electrolytes on casting slips and for the determination of the effects of method of preparation and treatment on casting behavior.

Distinct promise is also indicated for the objective design of casting bodies having prerequisite properties by the use of data obtained for various clays, although further experimental investigation on composite mixtures of two or more clays is needed in order to permit the more intelligent design of bodies in consideration of the properties indicated for the individual clays. This latter effort is required in view of the fact that mixtures of clays do not necessarily exhibit casting properties typical of the average properties of the individual clays. This statement does not mean that individual clays as used in body slips do not exhibit their characteristic properties but rather that the degree of effect may not be a proportionate function of the amounts present.

In addition to the usefulness of the methods evolved for application to casting clays and bodies, some of the tests could probably be used for the comparison and control of clays for plastic or dry-press bodies.

[24] R. Russell, Jr., "Development of Superduty Refractories from Ohio, Pennsylvania, and Kentucky Fire Clays," *Ohio State Univ. Eng. Expt. Sta. Bull.*, No. 105, 81 pp. (1940); *Ceram. Abs.*, **20** [4] 96 (1941).

Relative to the control which must be exercised in conducting these tests, it is sufficient to say that this effect depends largely on the degree of accuracy required. Many factors in slip preparation as well as test methods were found to influence the results obtained, but sufficient standardization may readily be effected without undue effort or complication to permit results of acceptable accuracy for all practical purposes. For the sake of reliability, duplicate test runs are recommended when there is any doubt as to the interpretation of a result or where close comparisons are required. In a majority of instances, however, a single test for any one property should suffice.

Because ball-clay and kaolin slips contain divergent amounts of water and because different weights of slip were used in conducting the casting tests by the Büchner funnel method, no direct comparisons could be made of the casting time and water retention between a ball clay and a kaolin. Where such comparisons are desired, it may be found expedient to select such quantities of slip that a standard amount of clay is used in the funnel in contrast with the foregoing procedure in which both specific gravity and quantity of slip differ according to the type of clay used. The water content of slip could also be standardized, in which case an amount of water (150%) as previously used in the ball-clay slips would be satisfactory. Errors, however, resulting from the settling of any particularly thin slips thus prepared should be avoided.

All tests were conducted on clay slips containing a substantial proportion of nonplastic constituent. This procedure is recommended not only because of the reduction in testing time involved but because of difficulties inherent in the handling of 100% clay slips and the forming of satisfactory specimens. Whereas 50 clay–50 flint mixtures were adopted as the standard for a majority of the tests herein reported and would be satisfactory for general clay testing, it is recommended for plant control that a nonplastic constituent of the amount and character employed in a production body of interest be used in combination with the clay or clays under consideration; for example, feldspar or other nonplastic would partially or totally replace the flint according to the body composition itself. Test results simulative of production expectancy would thus be obtained.

It might be advisable in routine testing to increase the amount of nonplastic beyond the 50–50 ratio and to use a larger Büchner funnel because a reduction of testing time would probably result without too great a sacrifice of reliability. This procedure is recommended only for standardized routine testing purposes.

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ENAMELED UTENSIL MANUFACTURERS' COUNCIL TENTATIVE STANDARD SOLUBILITY TEST FOR PORCELAIN ENAMELED COOKING UTENSILS*

By F. A. Petersen and A. I. Andrews

Abstract

The various methods for determining the degree of resistance of porcelain enameled cookingware to acid solubility are discussed. A method that overcomes many of the difficulties encountered in such a test and offers greater accuracy and reproducibility is described in detail.

I. Introduction

The present investigation was undertaken to develop a simple, accurate, and convenient method for determining the acid solubility of kitchenware and hospital-ware enamels.

Such a test method is needed because there is practically no correlation between the results now obtained in different laboratories. A review of the literature and considerable correspondence showed that the New South Wales test,[1] the *Good Housekeeping* test,[2] and the loss-in-weight test[3] were those most commonly used. There were, however, so many variations in the conditions under which these tests were conducted that even when the laboratories used the same test their results did not agree and could not be correlated.

II. Methods

After experimenting with the most popular and promising of the methods, the loss-in-weight test was selected, and the conditions for using it were standardized. The test sample was weighed, treated with a standard acid solution for a given time at boiling temperature, and reweighed to determine the loss, which was calculated in grams per square inch of surface exposed to attack.

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* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Enamel Division). Received May 15, 1943; revised copy received October 22, 1943.

[1] "Enamel Utensils—New South Wales Regulation," *Australian Food*, **7** [4] 19 (1937); *Ceram. Abs.*, **17** [2] 57 (1938).

[2] J. E. Hansen, ed., Manual of Porcelain Enameling, pp. 244–45. Enamelist Publishing Co., Cleveland, 1937. 520 pp.; *Ceram. Abs.*, **17** [2] 59 (1938).

[3] (*a*) L. Stuckert, "Stannic Oxide as Opacifier in Wet Enamels." *Internat. Tin Research Development Council Bull., Tech. Pub.*, **A65**, 26–36 (Oct., 1937); 81 pp.; *Ceram.* **17** [7] 246 (1938).

(*b*) E. E. Bryant, "Controlled Boiling Acid Test for Porcelain Enamels," *Jour. Amer. Ceram. Soc.*, **20** [10] 317–19 (1937).

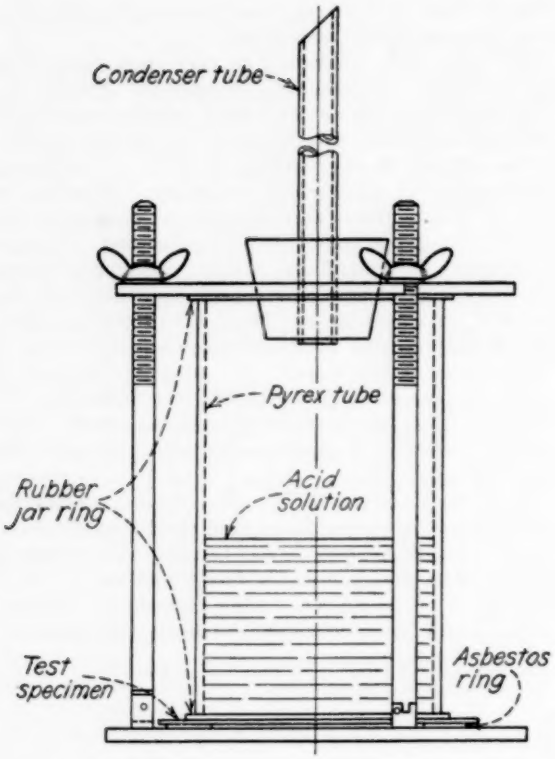

FIG. 1.—Solubility apparatus: Steel plate, 1/8 in. thick, for base and top plate; top plate also given coating of acidproof enamel; standard jar ring suitable for the rubber ring; asbestos sheeting, 1/16 in. thick, used for asbestos rings, which are 3 3/8 in. in diameter with center holes 2 1/4 in. in diameter.

III. Apparatus

The equipment used for the test is shown in Figs. 1, 2, 3, and 4. Figure 1 shows the details of the apparatus used for clamping a 2 1/2-in. diameter Pyrex-brand glass cylinder onto the 3 1/4-in. diameter test specimen, which is then used as the container for the acid solution. A standard rubber fruit-jar ring forms a seal between the glass cylinder and the specimen. The asbestos ring between the specimen and the assembly ring prevents the rubber ring from becoming so hot that it sticks to the specimen. A rubber jar ring is also used at the top of the glass cylinder, and the 14-in. condenser tube acts as a reflux. The test specimen can be stamped from the bottoms of production pans, or the enamel can be specially fired on 3 1/4-in. blanks.

Many methods for cutting specimens from pans were tried. The use of shears, a cold chisel, grinding wheels, or a cutting torch yields usable specimens, but the most convenient and satisfactory method is that of stamping. The punch and die shown in Fig. 2 is recommended because it gives a clean edge on all usable gauges of stock and on enamel thicknesses up to 0.025 or 0.030 in. The punched edges of the test specimen should be lightly rubbed with a fine file to remove any small loosely adhering chips of enamel.

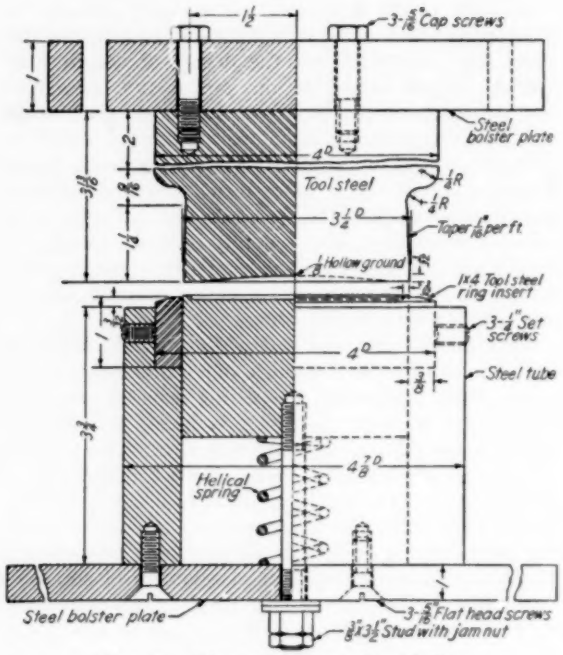

FIG. 2.—Diagram for punch and die.

Figure 3 shows the position of three specimens on a Heat-Flo SB-2000 115–120 volt, 2000-watt electric hot plate. This hot plate insures comparable results in different laboratories. The electrical wiring for control of the hot plate is shown in Fig. 4.

Directions for the solubility test follow.

(1) Preparation for Test

(1) Preheat the hot plate, with the high-heat switch on, for at least one hour at 500 watts.

(2) Prepare (fresh for each test) a 6% (by weight) citric acid solution and bring to boiling (keep covered with a watch glass to prevent loss from vaporization).

(3) Cut one circular plate, 3 1/4 in. in diameter, from each pan to be tested.

(4) File the edges of plates carefully with a triangular file to remove any loose chips.

(5) Wash the plates with soap and water and rinse with distilled water.

(6) Dry the plates at 220°F. for 10 minutes and cool to room temperature in a desiccator containing calcium chloride.

(7) Prepare three plates for each test.

(8) The surface of the test plate exposed to the test solution should be the inside bottom surface of the pan from which the test plate was cut.

(2) Procedure

(1) Remove the plates from the desiccator, holding at the edges; inspect the edges and remove any loose chips before the initial weighing.

(2) Weigh the plates on an analytical balance (to the fourth decimal place in grams).

(3) Place the asbestos gasket above the hole in the base plate of the solubility apparatus.

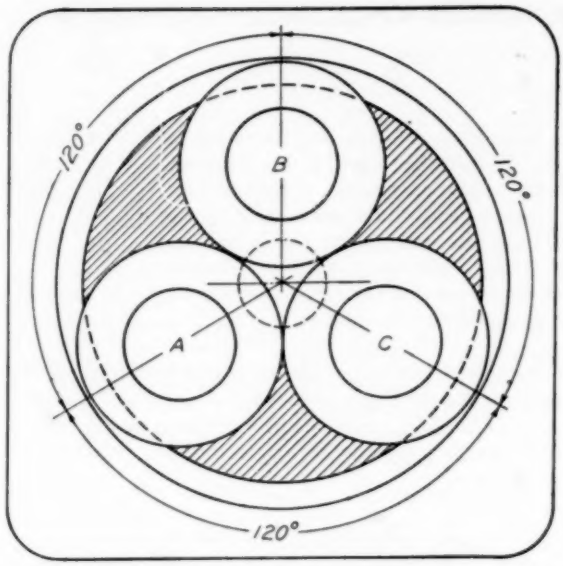

FIG. 3.—Position of test units on hot plate during test; shaded area, heating element of hot plate; areas within circles marked *A*, *B*, and *C*, areas of test plate exposed to acid attack.

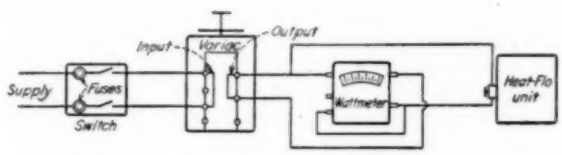

FIG. 4.—Electrical wiring for equipment.

(4) Place the test plate over the asbestos gasket.

(5) Place a rubber jar ring on the test plate and center the Pyrex-brand tube on the jar ring.

(6) Place another rubber jar ring on top of the Pyrex-brand tube and set the top plate on it.

(7) Set the clamping screws in position and tighten the wing nuts.

(8) Pour 150 cc. of the boiling citric acid test solution into the Pyrex-brand tube; place the glass condensing tube in position; and center the three units on the hot plate.

(9) After five minutes, reduce the watt input so that the test solution is at an active but not violent boil and continue test for 2 hours and 25 minutes (total heating period of $2^1/_2$ hours).

(10) At the end of this period remove units from the hot plate; remove the condensing tubes; pour out the solution; and rinse the apparatus with distilled water before disassembling it.

(11) Remove the test plates from units; rinse (do not scrub) with distilled water, and dry at 220°F. for 10 minutes; place in the desiccator while cooling to room temperature.

(12) After the plates are cooled to room temperature, weigh on an analytical balance.

(13) Calculate the weight loss per square inch of wetted area; *example*, 3.975 sq. in. wetted area.

Wt. before (gm.)	Wt. after (gm.)	Wt. loss (gm.)	Wt. loss (gm./in.²)	Diff. from avg. (%)
28.1356	28.1156	0.0200	0.0050	+6.4
29.1200	29.1010	.0190	.0048	+2.1
28.9300	28.9130	.0170	.0043	−8.5

$$\text{Avg. } \frac{0.0141}{3} = 0.0047.$$

(14) If the samples do not check within ±10% of the average, check three additional plates and compute the average, using all values that are within ±10% average.

(3) Precautions

(1) Remove any loose chips from edges of the test plates before the initial weighing.

(2) Use a freshly prepared test solution.

(3) Have the acid solution at boiling temperature before adding it to the test units.

(4) Time the test carefully, and do not neglect to reduce the wattage after the first five minutes.

(5) Rinse but do not scrub the test plate after it has been removed from the test unit.

(6) Cool the test plates in the desiccator to room temperature after drying at 220°F.

(7) Handle test specimens by the edges at all times.

Acknowledgment

This investigation was carried out in the Department of Ceramic Engineering at the University of Illinois and was financed by the Enameled Utensil Manufacturers' Council of Cleveland, Ohio.

The authors wish to express their appreciation to Mr. Zimmerman of the Fletcher Enamel Company of Dunbar, West Virginia, who suggested a similar test, and to the members of the technical Committee of the Council, E. C. Dexheimer, H. C. Arnold, E. H. Kelsey, B. S. Kirk, P. A. Mallonn, and A. J. Vollrath, for their advice, suggestions, and cooperation.

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CATAPHORESIS OF PURIFIED, FRACTIONATED KAOLINITE PARTICLES*

By W. L. Coughanour and J. L. Utter

Abstract

The cataphoretic velocity of three purified, monodisperse fractions of Florida kaolin was determined by the ultramicroscope method. The effect of particle size, kaolinite concentration, and electrolyte concentration on the migration velocity of the particles was observed. Calculations of zeta potential, charge density, and total charge were made for the various systems. It is shown that the zeta potential decreases with increasing particle size and increasing clay concentration. The plots of migration velocity versus electrolyte concentration follow the usual form for such curves, rising rapidly with the first electrolyte additions and flattening out as equilibrium is reached.

I. Introduction

It is a well-established fact that the origin of many important phenomena peculiar to clay may be traced to the surface charge exhibited by the clay particles when they are suspended in aqueous media.

The addition of electrolytes to a clay slip reduces by 60 to 80% the water content, which would otherwise be necessary for fluidity, thus greatly lessening the drying time and drying shrinkage of cast pieces.

The base-exchange capacity of soil clays, by means of which necessary elements are made available to growing plants,[1] is of prime importance to the soil chemist. The dewatering of clay slurries, moreover, is often conveniently accomplished by the application of an electrical potential.

These and many other properties of clays, which are commercially important and scientifically interesting, are directly dependent on the electrical nature of the clay particle surface and the consequent development of an electrical double layer around the particle when it is suspended in an aqueous media.

Knowledge of the exact origin of the surface charge is limited by the extent of the present information relating to the molecular structure of surfaces.[2] Several theories have been advanced, none of which as yet has been universally accepted. The lack of facts regarding the charge origin, however, does not appreciably hinder the determination of several other important quantities, namely, (1) the charge density of the surface and (2) the electrokinetic potential, ζ, across the diffuse double layer of the clay micelles.

To the extent of the authors' knowledge, no literature has been published in which these two values were determined for purified, monodisperse fractions of kaolinite. Hauser and LeBeau[3] obtained excellent data on purified, fractionated bentonite sols, and Jenny and Reitemeier[4] used dialyzed, unfractionated Putnam clay.

The object of the present work was to determine the effect on the electrical properties of purified, monodisperse kaolinite suspensions of variations in (1) NaOH concentration, (2) in clay concentration, and (3) in particle size.

II. Theoretical Considerations

Of the several means available for the study of electrophoresis, the microscope method was chosen as the most convenient for this work. The moving boundary method, which is the other procedure most widely used, is designed chiefly to study dissolved material,[5] whereas the microscope method is best for the observation of individual particles. Various other advantages offered by the microscopic method are listed as follows:[5] (1) a single determination may be made very rapidly; (2) during the period of observation, the environment of the particle does not appreciably change; (3) any differences in the electric mobility of various particles in the field may be simultaneously observed; and (4) measurements may be made in extremely dilute solutions.

Because the size range of the particles studied varied from 0.2 to 1.6 microns, a slit ultramicroscope was used so that the smaller particles would be clearly visible. The cell was the same as that used and described by Hauser and LeBeau.[3] The ratio of the applied e.m.f. to the actual e.m.f. across the cell chamber was determined by the Northrup-Kunitz method.[6] Smoluchowski's[7] equation was applied in determining the depth of focus necessary to eliminate the effects of the electroosmotic flow of the liquid[8] in the cell.

Any attempt to obtain zeta-potential values from the migration speed of the particles involves a careful consideration of the possible formulas to determine which

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* For presentation at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (White Wares Division). Received January 15, 1944.

[1] W. P. Kelley, "Modern Clay Researches in Relation to Agriculture," *Jour. Geol.*, **3** [3] 307–19 (1942); *Ceram. Abs.*, **21** [8] 177 (1942).

[2] H. Mueller, "Theory of Electrophoretic Migration," *Annals N. Y. Acad. Sci.*, **39,** 111–20 (1939).

[3] E. A. Hauser and D. S. LeBeau, "Studies in Colloidal Clays, II," *Jour. Phys. Chem.*, **45** [1] 54–64 (1941); *Ceram. Abs.*, **21** [3] 68 (1942).

[4] Hans Jenny and R. F. Reitemeier, "Electrokinetic Properties in Relation to Base-Exchange Phenomena," *Jour. Phys. Chem.*, **39,** 593 (1935).

[5] H. A. Abramson, "Determination of Electrical Charge of Surfaces by Microscope Method of Electrophoresis," *Annals N. Y. Acad. Sci.*, **39,** 121–47 (1939).

[6] J. N. Northrup and M. Kunitz, "Improved Type of Electrocataphoresis Cell," *Jour. Gen. Physiol.*, **7,** 729 (1925).

[7] M. Smoluchowski, Handbuch der Electricität und des Magnetisimus, Vol. 2, p. 366. Barth, Leipzig, 1921.

[8] (*a*) G. Quincke, *Pogg. Ann.*, **107,** 1 (1859).
(*b*) R. Ellis, "Eigenschaften der Olemulsionen und die elektrische Ladung," *Z. Phys. Chem.*, **78** [12] 321–53 (1911).

one is most applicable to the particular system being studied.

Mueller[2] has shown that Stokes' law is not valid for particles surrounded by a double layer because it takes into account only the viscous resistance of the currents created by the particle itself and neglects the resistance offered by the movement of the outer charges.

Formula (1) of Debye and Hückel[9] applies, according to Mooney[10] and Henry,[11] only in cases of extremely small particles and very dilute solutions.

$$V = \frac{DX\zeta}{6\pi\eta} \tag{1}$$

V = migration speed.
D = dielectric constant of medium.
ζ = zeta potential.
η = viscosity of liquid.
X = applied electric field.

$$V = C\frac{DX\zeta}{\eta} \tag{2}$$

The Smoluchowski equation (2) at present is probably the best general formula for most purposes. The factor, $C = \frac{1}{4\pi}$, according to Smoluchowski[7] is independent of the particle size. Debye and Hückel,[9] moreover, more recently have stated that such a constant applies to cylindrical particles, whereas the factor, $\frac{1}{6\pi}$, is applicable to spherical particles. Because the most logical shape for clay particles is cylindrical and other factors in the two formulas are equal, Smoluchowski's equation was used. According to Mueller,[2] however, it is questionable that any of the present formulas give absolute values of zeta potentials which are completely accurate. With this in mind, the values obtained in this study are considered in the relative sense and not as absolute quantities.

As stated previously, Stokes' law does not apply to particles possessing double layers because the resistance to flow or acting force on the particle is made up of two factors, namely, the resistance of the liquid proper and the additional resistance of the outer charges which move in a direction opposite to that of the particle. The latter factor is extremely difficult to evaluate, and the use of a different equation to obtain the charge density of the particles was therefore indicated. Formula (3), which was developed by Abramson,[5] was used.

$$\sigma = \sqrt{\frac{NDKT}{2\pi \times 1000}}\, C_1 Z_1 \left[\frac{1}{Z_2}\left(e^{Z_2\frac{E\zeta}{KT}} - 1\right) + \frac{1}{Z_1}\left(e^{-Z_1\frac{E\zeta}{KT}} - 1\right)\right] \tag{3}$$

σ = charge density.
N = Avogadro's No.
K = Boltzmann's constant.
T = absolute temp.
c = molar concentration.
e = base of natural log.
E = electronic charge.
Z_1 and Z_2 = respective valence of ions.

In case $Z_1 = -Z_2 = Z$, equation (3) reduces to equations (4) or (5).

$$\sigma = 2\sqrt{\frac{NDKT}{2\pi \times 1000}}\sqrt{C}\sinh Z\frac{E\zeta}{2KT} \tag{4}$$

$$\sigma = 2\alpha\sqrt{C}\sinh\frac{Z\zeta}{2\beta} \tag{5}$$

α = 17,650.
β = 0.025 volt at 18°C.

The original charge on the particles resulting from the dissolved CO_2 present in the water was calculated from equation (3), and this value in each case was subtracted from the total charge density.

III. Experimental Procedure

(1) Preparation of Clay Suspensions

The clay used was Florida kaolin which had been leached and dialyzed according to the method given by Norton and Johnson.[12] This process removes most of the organic and inorganic salts which were originally present in the clay and which could conceivably interfere with the present values.

Monodisperse fractions, in microns, of 0.2 to 0.4, 0.4 to 0.8, and 0.8 to 1.6 were obtained by means of the ultracentrifuge as described by Norton and Speil.[13]

The size range of the fractions had been checked by Stokes' law, employing a long-arm centrifuge to shorten the settling time of the particles. This procedure is the same as that followed by Norton and Speil.[14]

The clay suspensions used in the experiment were prepared by determining first the percentage of clay in the dialyzed, fractionated base slip. The amount of base slip calculated to produce the desired concentration was measured to 0.01 cc. with a 1-cc. pipette. In a similar manner, the required amount of standardized NaOH was measured and added to the slip. Water was then added in sufficient quantity to bring the total weight of clay, electrolyte, and water to the correct value required for the concentration desired.

The percentage concentrations of clay, based on dry weight, were 0.001, 0.004, 0.007, and 0.01. The amount of NaOH added was calculated in terms of milliequivalents per 100 gm. of dry clay. This is merely a method of expressing the concentration of electrolyte and, as far as this experiment is concerned, has nothing to do with the base-exchange capacity of the clay.

The solutions were agitated, and all samples were aged for four days before any mobility determinations were made.

(2) Observations of Migration Speeds

Before any observations were made, the ultramicroscope and side cells were carefully balanced so that there

[9] P. Debye and E. Hückel, "Bemerkungen zu einem Latze über Kataphoretische Wanderunggeschwindigkeit suspentieter Teilchen," *Physik Z.*, **25** [2] 49–52 (1924).

[10] Melvin Mooney, "Electrophoresis and the Diffuse Ionic Layer," *Jour. Phys. Chem.*, **35** [1] 331–44 (1931); *Ceram. Abs.*, **10** [3] 226 (1931).

[11] D. C. Henry, "Cataphoresis of Suspended Particles: I, Equation of Cataphoresis," *Proc. Roy Soc.* [London], **A133** [821] 106–30 (1931); *Ceram. Abs.*, **12** [1] 37 (1933).

[12] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: I, Preparation of Purified Kaolin Suspension," *Jour. Amer. Ceram. Soc.*, **24** [2] 64–69 (1941).

[13] F. H. Norton and S. Speil, "Fractionation of Clay into Closely Monodispersed Systems," *ibid.*, **21** [10] 367–70 (1938).

[14] F. H. Norton and S. Speil, "Measurement of Particle Sizes in Clay," *ibid.*, **21** [3] 89–97 (1938).

TABLE I

SUMMARY OF RESULTS WITH VARIED NaOH CONCENTRATION*

Base (m.e.)/100 gm. clay	(A) Migration velocity (μ/sec./volt/cm.) 0.2–0.4 μ	0.4–0.8 μ	0.8–1.6 μ
0	4.17	4.17	4.10
50	5.23	5.23	4.83
250	5.59	5.47	5.35
500	6.47	6.15	6.00
750	6.65	6.47	6.15
1000	6.84	6.65	6.31
3000	7.03	6.84	6.65
5000	7.03	7.03	6.84
	(B) Zeta potential (mv.)		
0	48.3	48.3	47.5
50	60.7	60.7	55.8
250	64.8	63.4	61.9
500	75.0	71.3	69.5
750	77.1	75.0	71.3
1000	79.3	77.1	73.2
3000	81.5	79.3	77.1
5000	81.5	81.5	79.3

* 0.001% clay concentration.

was no flow of the medium in the cell caused by a difference in level from one side to the other.

The zinc electrodes were immersed in a 50% $ZnSO_4$ solution, which by means of stopcocks was prevented from flowing into the cell proper.

Illumination was provided by a carbon arc lamp equipped with a mechanical electrode feed which afforded an arc of fairly constant intensity. The light from the arc was passed through a slit system and brought to focus on the cell in the desired working range.

Actual observations of the migration speeds of the particles were made by completely filling the cell and side tubes and eliminating all air bubbles. An e.m.f. of 90 volts, supplied by two B batteries, was impressed across the zinc electrodes, and the movement of a single particle as it passed one division on the ocular scale was timed with a stopwatch, which was accurate to $^1/_5$ second and which could be estimated to $^1/_{10}$ second. After the speed of several particles was observed, the polarity of the electrodes was reversed and the mobility of the particles in the opposite direction was noted. Only those readings were used which were the same in both directions for a given sample. A total of ten readings in each direction was taken for each sample, and the results in each case were averaged. After the completion of observations on each sample, the cell was flushed out with distilled water and the e.m.f. of the B batteries was checked.

IV. Discussion of Results

(1) Comparison with Previous Investigations

In attempting to compare the results obtained here with those of other investigators, it must be remembered that the many variables, such as clay concentration, electrolyte concentration, particle size, and formulas, will necessarily be at variance in any two studies. One investigator may find it more convenient to work in a certain particle-size range or may decide that a certain formula is better suited to the individual case than some other formula previously used. With these facts in mind, the following comparisons may be made:

TABLE II

SUMMARY OF RESULTS WITH VARIED CLAY CONTENT*

Clay (%)	(A) Migration velocity (μ/sec./volt/cm.) 0.2–0.4 μ	0.4–0.8 μ	0.8–1.6 μ
0.001	6.61	6.28	6.23
.004	6.61	6.13	6.05
.007	6.61	6.05	5.91
.01	6.61	5.98	5.91
	(B) Zeta potential (mv.)		
0.001	75	71.7	69.8
.004	75	69.8	68.9
.007	75	68.9	67.5
.01	75	68.2	67.5

* 500 m.e. base added.

From Tables I and II, the zeta potentials obtained are shown to vary from 48.3 to 81.5 mv., depending on the electrolyte concentration, clay concentration, and particle size.

Hauser and LeBeau[3] added no electrolyte in their investigations with bentonite, and the largest particle size used was 0.096 micron. In this size range, zeta potentials of 59 to 84 mv. were obtained. The closest comparison of conditions that can be made in this study was in the 0.2 to 0.4 μ size range with no added electrolyte where an average value of 48.3 mv. was obtained. This value was reached when the clay concentration was 0.001%, whereas the potentials determined by Hauser and LeBeau were obtained in clay concentrations varying from 0.210 to 0.742%.

Jenny and Reitemeier,[4] working with unfractionated clay at a NaOH concentration of 50 m.e. and clay concentrations in the same range as used by the authors, obtained an average value of 57.6 mv. For the various fractions used in the present work, the zeta potentials were as follows:

μ	NaOH (m.e.)	Mv.
0.2– 0.4	50	60.7
0.4– 0.8	50	60.7
0.8–01.6	50	55.8

Although these values appear to check quite closely with the average results of Jenny and Reitemeier,[4] they were obtained by using the factor $\frac{1}{4\pi}$ in the Smoluchowski equation, whereas Jenny and Reitemeier used the factor $\frac{1}{6\pi}$. On a comparative basis, therefore, the values presented here would be somewhat higher than those obtained by Jenny and Reitemeier.[4] Because the order of magnitude of the results in the investigations compared here is the same, the differences noted may easily be caused by the fact, as previously stated, that the controllable variables in the three studies were not coincident.

(2) Interpretation of Data

Figure 1 shows the relationship between the rate of migration of the particles and the concentration of

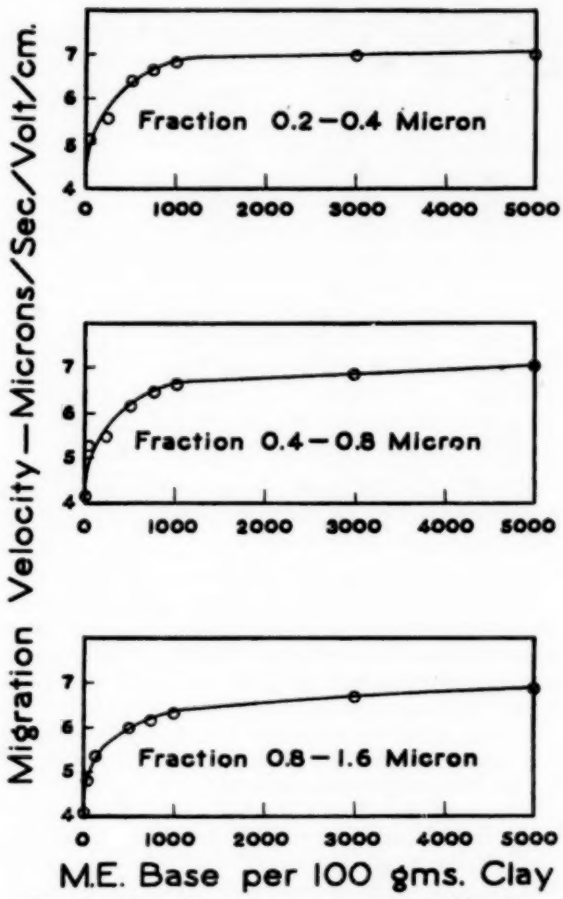

FIG. 1.—Migration rate vs. concentration of NaOH.

NaOH for the three fractions studied. These plots conform to the usual ζ-concentration curves for univalent electrolytes. The first point represents the clay in the dialyzed state before any electrolyte has been added. The charge on the particle in this condition is partially due to the dissolved CO_2 in the water and partially to the unremoved impurities and natural "structural" charges on the clay particle.

As the concentration of the base is increased, the curve rises rapidly until about 1000 m.e. have been added. The curve then flattens out, indicating that the surface charges of the particles, probably resulting from the broken, unsaturated lattice structure, have been almost satisfied by absorption of the OH^- ion from the medium, and the rate of absorption has been reduced almost to an equilibrium point. If the addition of electrolyte had been carried beyond the range studied, the excess of NaOH would eventually have forced an influx of Na^+ ions close to the particle surface, resulting in a neutralization of the OH^- ions originally absorbed and a consequent flocculation of the system.

In Fig. 2, the rate of migration is plotted against particle size for the various clay concentrations studied. The electrolyte concentration for this series of curves was 500 m.e. in all cases.

In every case, the rate of migration, which is directly

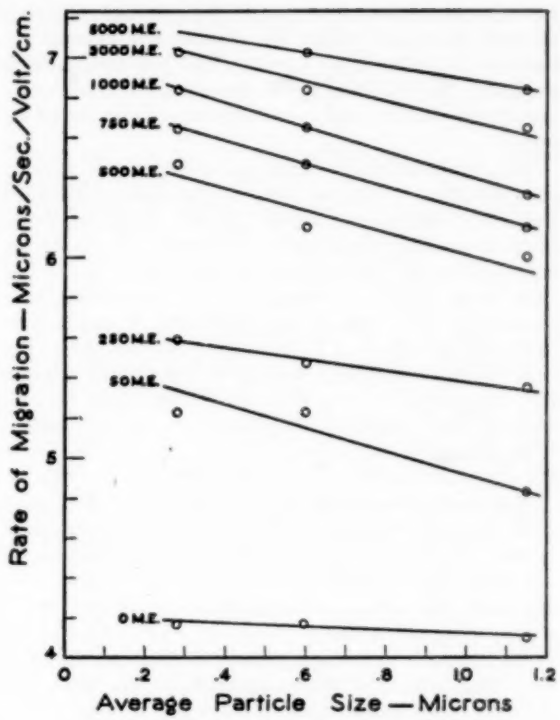

FIG. 2.—Migration rate vs. particle size.

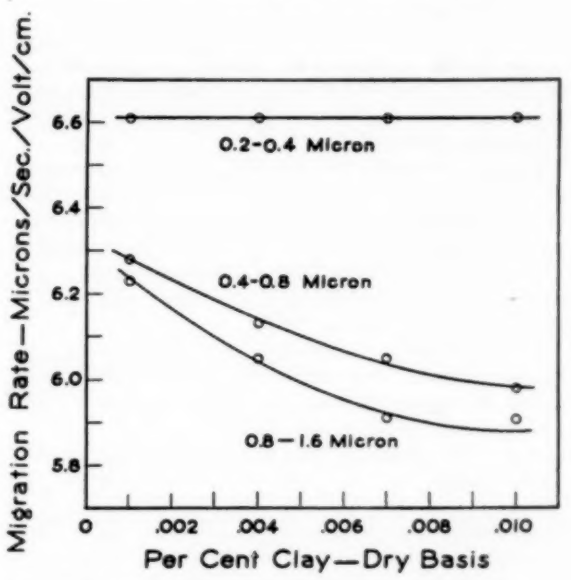

FIG. 3.—Migration rate vs. percentage of clay.

proportional to the zeta potential, decreases with increasing particle size. Hauser and LeBeau,[3] working with bentonite, obtained similar results which they explained in a logical manner.

Bentonite particles consist of flat, platelike parcels stacked one upon the other along the c axis of the lattice. Because only the ions of the free surfaces are responsible for the formation of the double layer of the

particles as a whole, the greater the number of parcels stacked upon each other, the smaller will become the number of double-layer forming ions per unit particle surface. As the size of the bentonite particle increases, the charge density and therefore the zeta potential decrease.

This explanation, however, according to the most recent theories, would not hold in the case of kaolinite particles. Although kaolinite consists of flat, platelike particles similar to bentonite, it depends only on the unsaturated edges and corners as adsorption areas and derives no additional charge, as does bentonite, from the larger, flat surfaces perpendicular to the c axis. With this in mind, the stacking of parcels upon each other with a consequent increase in size should cause no loss whatsoever of "active" or double-layer forming surfaces and therefore no change in electric mobility with increasing size unless some change also occurs on the edges and corners of the parcels.

If a single large particle is considered to be broken down into smaller particles by natural or applied forces, it seems logical to assume that many fractures would occur parallel, or nearly so, to the c axis in addition to the basal cleavages. Such fractures would give rise to a very irregular surface on one or more edges of the broken particle, causing a greater surface per unit area than that possessed by the original particle and consequently more unsaturated bonds able to adsorb ions from the medium. The fact that sharp edges and corners act as "charge concentration" points gives further credence to this possibility. This increase in surface per unit area and addition of "concentration" points would continue as the particle was progressively fractured, the net result being a greater charge density apparent with the smaller particles and a resultant higher zeta potential.

Figure 3 shows the relation between the percentage of clay and the rate of migration. With the exception of the 0.2 to 0.4 μ fraction, the rate of migration decreases with increasing clay concentration. The explanation of Hauser and LeBeau,[3] who obtained similar results with higher concentrations and smaller particles, fits the present data satisfactorily.

As the clay concentration is increased, the particles become crowded together more closely, resulting eventually in a compression of the electrical double layers and a consequent decrease in zeta potential.

Table III (*A* and *B*) lists the charge density and the total charge on the particles, respectively. The charge density was obtained from formula (5), and the total charge was obtained by multiplying these values times the apparent side area of the assumed cylindrical particle shape, using a value of $^1/_{12}$ the diameter as the cylinder height. The use of the side area only as the region of charge distribution is based on recent data and theory which indicate this to be a logical assumption. Values of total charge roughly thirteen times as great are obtained if the total area of the particle is used.

TABLE III

CHARGE DENSITY AND TOTAL CHARGE ON PARTICLES

Base (m.e.)/100 gm. clay	0.2–0.4 μ	0.4–0.8 μ	0.8–1.6 μ
	(*A*) Net charge density (e.s.u./cm.^{2})		
0	57*	57*	55*
50	67	67	61
250	244	231	225
500	477	436	417
750	679	593	545
1000	807	729	663
3000	1445	1390	1305
5000	1885	1885	1795
	(*B*) Total charge on particle (e.s.u. × 10^9)		
0	1.35	5.37	21.5
50	1.58	6.30	23.0
250	5.52	21.8	85.0
500	11.2	41.0	157.0
750	16.0	54.8	206.0
1000	19.0	68.6	250.0
3000	34.1	131.0	492.0
5000	44.5	177.0	677.0

* Charge due to dissolved CO_2 gas; this value was used in determining the rest of the net charge due to added NaOH.

V. Conclusions

The present studies have shown that the surface charge affects many important phenomena connected with kaolinite–water systems. Although these measurements give information on the zeta potential relating to size, concentration of solids, and NaOH, it has not been definitely ascertained what relationship, if any, exists between the total charge and the zeta potential which were measured in this work.

The conclusions based on these results are tentative and rather incomplete, pending future work; they may, however, be listed as follows: (1) The zeta potential increases with decreasing particle size owing to increased surface per unit area on the fractured edges. (2) The zeta potential increases with an increase in concentration of NaOH to a point where the unsaturated bonds are completely satisfied. (3) The zeta potential decreases, except in the case of the smallest fraction, with increased clay concentration.

The practical significance of this work is perhaps not readily apparent at this time. That the zeta potential increases in magnitude with a decrease in particle diameter has now been proved. This fact will be important in studies on casting slips made from size-controlled clays. These data may also be helpful in the interpretation of the causes of the charge on the particle. In a theoretical sense, the data contribute to the store of knowledge concerning the colloidal properties of clay.

Acknowledgment

The authors wish to express their appreciation to F. H. Norton, E. A. Hauser, D. S. LeBeau, and H. Mueller for helpful advice and suggestions. Grateful acknowledgment is also made to E. A. Hauser for the use of the ultramicroscope equipment.

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OPTICAL FLUOR-CROWN GLASSES*

By Walter A. Fraser and Lee O. Upton

Abstract

The effect of variations in composition on optical properties was studied. The index of refraction is lowered by the substitution of fluorine and alumina for silica; the reciprocal dispersion, however, is increased by fluorine and lowered by alumina so that fluorine and alumina can be balanced against each other to give almost any desired optical properties within the field investigated, that is, in the range of 1.46 to 1.50 for index of refraction and 63 to 70 for the reciprocal dispersion.

I. Introduction

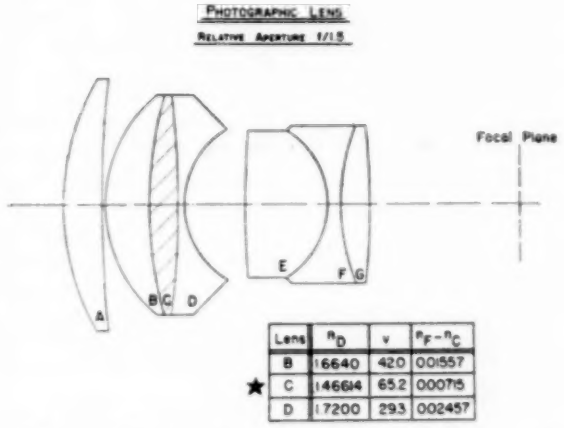
The use of fluorine as an optical glass constituent may have been suggested by the fact that certain fluorine-containing minerals, such as fluorite, have unusual optical properties that are useful to the optical designer. In fact, fluorite itself is used as an optical element in highly corrected microscope objectives.

About 1910, Gifford[1] described a quartz-fluorite combination which gave an exceptionally fine achromatic lens, producing a perfectly flat field for the whole spectrum into the ultraviolet.

Previous to the start of the present World War, all fluor-crown glasses were imported from Europe, and although the quantity used was not large, these glasses have important uses in certain types of optics. In order to make this country independent of the European supply, an investigation of fluor-crown glasses was made. A glass with an index of refraction of 1.4645 and a reciprocal dispersion of 65.7 was sought, but the investigation was not limited to the development of this one glass. The future requirements for other optical fluor-crown glasses were considered in this study, and a thorough investigation was made although it was not intended to be exhaustive.

Very little information has been published on the use of fluorine in optical glasses. Morey[2] gives the compositions and optical properties of two glasses made by Chance in England and Parra-Mantois in France. The optical properties of a glass made by Schott and Genossen are also given, and the oxides present are listed but the percentage composition is not indicated. Hovestadt[3] mentions only the possible use of fluorine and its general effect on the dispersion of a glass, and Knapp[4] lists the optical properties and composition of a fluor-crown glass.[5]

An example of the use of a fluor-crown glass in a photographic lens of relative aperture f–1.5 is shown in Fig. 1. In this particular lens, it is used in the C element between two glasses of high index of refraction. The large difference in indices of refraction at the two boundaries of the C lens determines the curvature of the two surfaces. These curvatures, in combination with the index differences, determine the zonal spherical aberrations for the entire field. This glass makes possible a quality of image in a lens of this type that could not be obtained otherwise.



	Lens	n_D	v	$n_F - n_C$
	B	1.6640	42.0	0.01557
★	C	1.46614	65.2	0.00715
	D	1.7200	29.3	0.02457

Fig. 1.—Example of use of a fluor-crown glass used in the C element to give corrections which could not be obtained with any other type of glass.

II. Experimental

(1) Method of Introducing Fluorine into Batch

Different fluorine-bearing chemicals were tried to determine those most suitable for introducing the fluorine into the batch. Calcium fluoride, as well as other compounds containing divalent elements, could not be used because of their tendency to produce opalescence. The sodium fluorides could not be used because sodium gives too high an index and also causes opalescence. Anhydrous KF introduced too much potash for the amount of fluorine desired, thus reducing the available

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Glass Division). Received November 26, 1943.

[1] J. W. Gifford cited in Spectroscopy by E. C. C. Baly, Vol. I, p. 92. Longmans, Green, and Co., London, 1924. 298 pp.

[2] G. W. Morey, Properties of Glass, pp. 408–11. Amer. Chem. Soc. Monograph Series, Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

[3] H. Hovestadt, Jena Glass and Its Scientific and Industrial Applications, p. 10 (tr. by J. D. and Alice Everett). Macmillan & Co., London, 1902.

[4] Oscar Knapp, "Optical Glass," *Glass Ind.*, **19** [12] 465–68 (1938); *Ceram. Abs.*, **18** [5] 125 (1939).

[5] Since this paper was prepared, a patent application by E. Berger and O. Freundel (Alien Property Custodian, Serial No. 395, 364, May 11, 1943) was published by the Alien Property Custodian giving the oxide compositions of a number of fluor-crown glasses. Most of these glasses have compositions outside the field of this investigation, containing approximately 20% of alumina as compared to a maximum of 15% of alumina in the glasses studied.

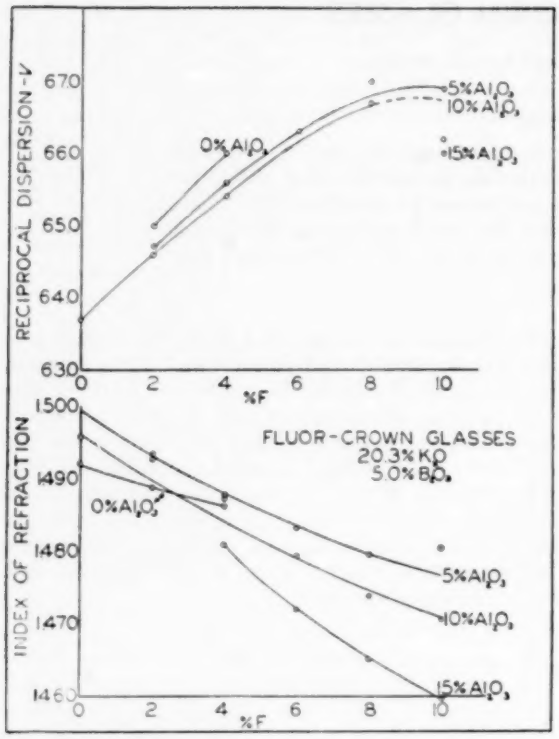


FIG. 2.—Composition versus optical properties of fluor-crown glasses containing 20.3 K_2O and 5.0 B_2O_3.

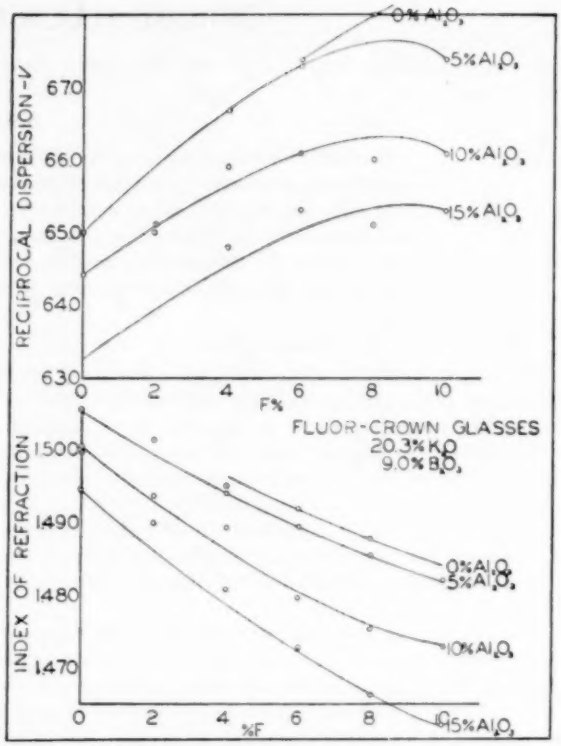


FIG. 3.—Composition versus optical properties of fluor-crown glasses containing 20.3 K_2O and 9.0 B_2O_3.

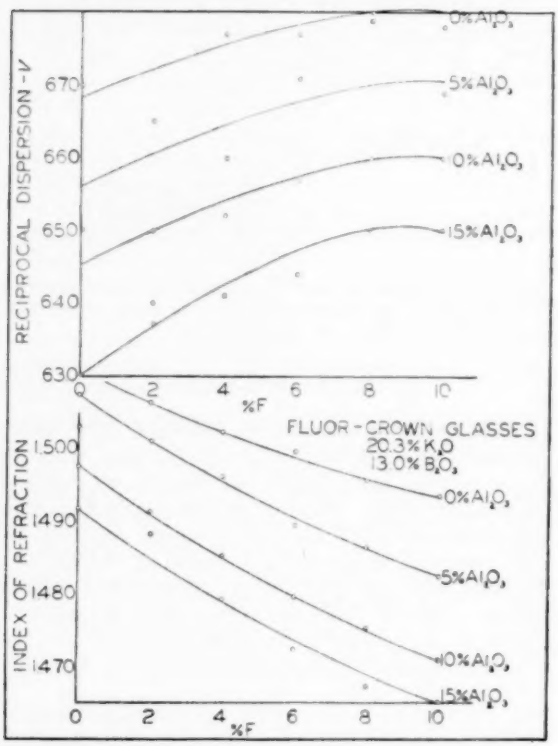


FIG. 4.—Composition versus optical properties of fluor-crown glasses containing 20.3 K_2O and 13.0 B_2O_3.

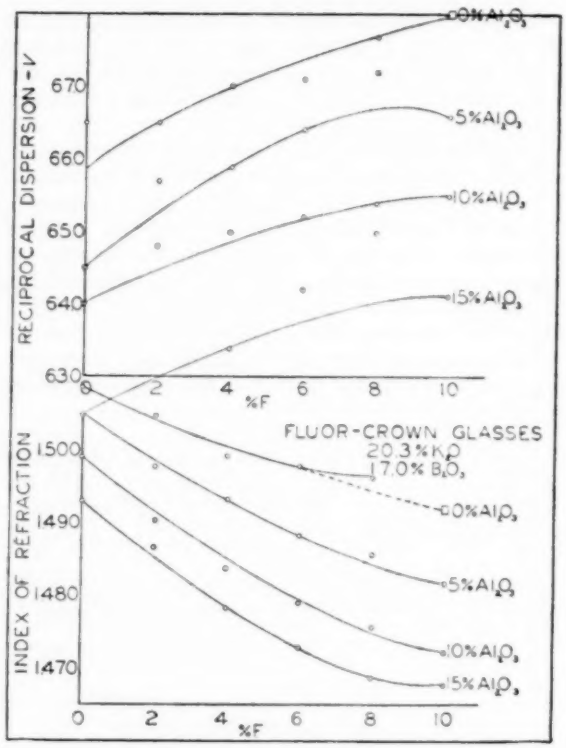


FIG. 5.—Composition versus optical properties of fluor-crown glasses containing 20 3 K_2O and 17.0 B_2O_3.

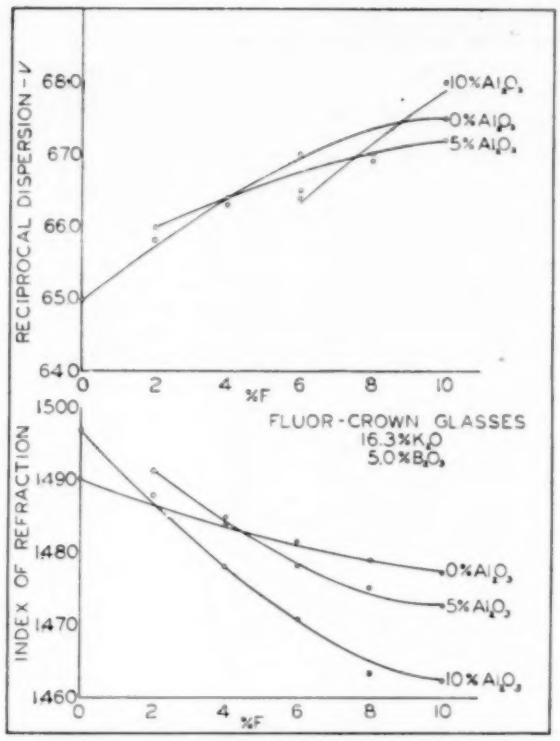


FIG. 6.—Composition versus optical properties of fluor-crown glasses containing 16.3 K_2O and 5.0 B_2O_3.

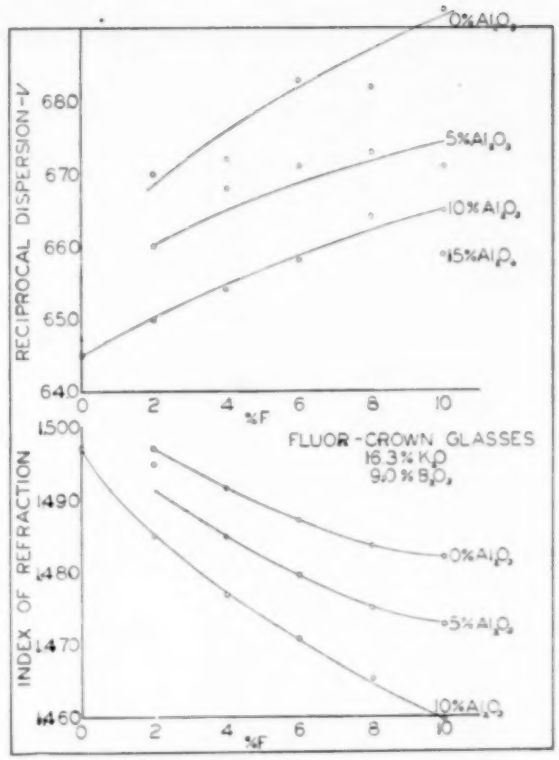


FIG. 7.—Composition versus optical properties of fluor-crown glasses containing 16.3 K_2O and 9.0 B_2O_3.

potash to be used as carbonate and nitrate, which are desirable for fining; $AlF_3 \cdot 3\frac{1}{2}\ H_2O$ and KHF_2 were therefore finally chosen for use. For reasons to be shown later, however, KHF_2 was the only source of fluorine used in preparing the small experimental batches.

The compositions listed in the literature are shown only as oxide compositions, and no indication is given as to the manner of introducing the fluorine into the batches.* The specific use of potassium acid-fluoride as a good means of introducing fluorine into a batch has never been found by the authors in a literature survey.

(2) Batch Compositions

The chemicals used for the preparation of the batches were the same as those used in the factory for the production of optical glass. No purification of the chemicals was made and grain size was not noted. The fluorine was introduced as KHF_2 in all the series, whereas $AlF_3 \cdot 3\frac{1}{2}\ H_2O$ was used only in some trial melts to check results. The remainder of the potassium oxide was divided between carbonate and nitrate for fining. Aluminum hydrate, boric acid, arsenic trioxide, and sand were the other chemicals used.

The batches were weighed into quart bottles and shaken thoroughly by hand. Because some of the batches had a tendency to "cake" if allowed to stand overnight, each one was weighed just previous to melting.

The compositions of the glasses shown in the graphs are given in Tables I and II, all substitutions being made for silica in weight percentages.

(3) Melting Procedure

All melts were made in a small tangential gas-fired furnace, using 3-in. diameter clay pots of approximately 1-lb. capacity. No unusual melting procedure was followed except that series of six melts each were arranged so as to assure comparable melting and atmospheric conditions from melt to melt within each series. No particular attempt was made to control precisely the atmospheric conditions in the furnace; the best temperature control, however, was possible when a neutral to slightly oxidizing atmosphere was maintained. The total melting time required was usually about four hours, which proved to be sufficient to obtain well-fined glasses. All melts were cast, rolled, lehr-annealed, and cut up into samples for grinding and polishing.

Indices and dispersions of each sample were then measured on the Pulfrich refractometer or on the Abbe refractometer, depending on the quality of the sample. Those too poor to be read on the Abbe refractometer were checked for index only by the liquid immersion method.

* The use of KF is mentioned by Berger and Freundel (see footnote 5).

TABLE I

PERCENTAGE COMPOSITIONS* AND PROPERTIES OF FLUOR-CROWN GLASSES

Glass	No.	SiO_2	F	B_2O_3	Al_2O_3	Index of refraction (N_D)	Reciprocal dispersion $\left(\frac{N_D - 1}{N_F - N_C}\right)$
5-0	1	74.6	0	5	0	1.492 L	
	2	72.6	2	"	"	1.4886	65.0 A
	3	70.6	4	"	"	1.4871	66.0
	4	68.6	6	"	"	1.4856 L	
	5	66.6	8	"	"		
	6	64.6	10	"	"		
5-5	1	69.6	0	"	5	1.4958	63.7
	2	67.6	2	"	"	1.4931	64.6
	3	65.6	4	"	"	1.4876	65.4
	4	63.6	6	"	"	1.4830	66.3
	5	61.6	8	"	"	1.4795	67.0
	6	59.6	10	"	"	1.4805	66.9
5-10	1	64.6	0	"	10	1.496 L	
	2	62.6	2	"	"	1.4927	64.7
	3	60.6	4	"	"	1.4862	65.6
	4	58.6	6	"	"	1.4793	66.3
	5	56.6	8	"	"	1.4736	66.7
	6	54.6	10	"	"	1.4706	66.2
5-15	1	59.6	0	"	15		
	2	57.6	2	"	"		
	3	55.6	4	"	"	1.481 L	
	4	53.6	6	"	"	1.472 L	
	5	51.6	8	"	"	1.465 L	
	6	49.6	10	"	"	1.4596	66.0
9-0	1	70.6	0	9	0		
	2	68.6	2	"	"		
	3	66.6	4	"	"	1.495 L	
	4	64.6	6	"	"	1.4917	67.4
	5	62.6	8	"	"	1.4878	68.0 A
	6	60.6	10	"	"	1.4823	69.0 A
9-5	1	65.6	0	"	5	1.5054	65.0 A
	2	63.6	2	"	"	1.5012	65.1
	3	61.6	4	"	"	1.4939	66.7
	4	59.6	6	"	"	1.4894	67.3
	5	57.6	8	"	"	1.4856	67.1
	6	55.6	10	"	"	1.4821	67.4
9-10	1	60.6	0	"	10	1.5007	64.4
	2	58.6	2	"	"	1.4937	65.0 A
	3	56.6	4	"	"	1.4891	65.9
	4	54.6	6	"	"	1.4796	66.1
	5	52.6	8	"	"	1.4753	66.0
	6	50.6	10	"	"	1.4728	67.1
9-15	1	55.6	0	"	15	1.4945	62.0 A
	2	53.6	2	"	"	1.4898	63.5
	3	51.6	4	"	"	1.4807	64.8
	4	49.6	6	"	"	1.4727	65.3
	5	47.6	8	"	"	1.4663	65.1
	6	45.6	10	"	"	1.4618	65.3

* K_2O, 20.3% throughout; As_2O_3, 0.1% throughout.

III. Results

The optical properties and chemical compositions of the glass batches are listed in Tables I and II. The variations of optical properties with the batch compositions are also shown graphically in Figs. 2 to 9.

(1) Effect of Fluorine

The substitution of fluorine for silica on a weight percentage basis lowers the index of refraction and raises the reciprocal dispersion in all cases, as may be seen in the figures, where the optical properties are plotted against the original batch compositions. The optical properties are not a linear function of batch composition because of the unequal loss of fluorine within each individual series.

The correlation between optical properties and batch compositions for melts of different sizes may be seen in Fig. 5, where the optical properties of a melt made in a 15-in. diameter clay pot (containing approximately 75 lb. of glass) are plotted with those of the 3-in. melts. The plot of the index of refraction and the reciprocal dispersion versus composition lie on the curves of the corresponding series of the smaller melts. The glass containing 10% of fluorine and 0% of alumina is plotted as a square to indicate that it is a larger melt.

TABLE I (*concluded*)

Glass	No.	SiO_2	F	B_2O_3	Al_2O_3	Index of refraction (N_D)	Reciprocal dispersion $\left(\frac{N_D - 1}{N_F - N_C}\right)$
13-0	1	66.6	0	13	0	1.5073	67.0
	2	64.6	2	"	"	1.5062	66.5
	3	62.6	4	"	"	1.5024	67.7
	4	60.6	6	"	"	1.4997	67.7
	5	58.6	8	"	"	1.4959	68.0
	6	56.6	10	"	"	1.4936	67.8
13-5	1	61.6	0	"	5	1.5031	64.0 A
	2	59.6	2	"	"	1.5010	64.0 A
	3	57.6	4	"	"	1.4962	66.0 A
	4	55.6	6	"	"	1.4897	67.1
	5	53.6	8	"	"	1.4866	67.9
	6	51.6	10	"	"	1.4827	66.9
13-10	1	56.6	0	"	10	1.4975	65.0 A
	2	54.6	2	"	"	1.4913	65.0
	3	52.6	4	"	"	1.4854	65.2
	4	50.6	6	"	"	1.4797	65.7
	5	48.6	8	"	"	1.4755	66.0
	6	46.6	10	"	"	1.4710	65.0 A
13-15	1	51.6	0	"	15	1.4916	63.0 A
	2	49.6	2	"	"	1.4882	63.7
	3	47.6	4	"	"	1.4793	64.1
	4	45.6	6	"	"	1.4727	64.4
	5	43.6	8	"	"	1.4671	65.0
	6	41.6	10	"	"	1.4650	64.9
17-0	1	62.6	0	17	0	1.5086	66.2
	2	60.6	2	"	"	1.5048	66.5
	3	58.6	4	"	"	1.4992	67.0
	4	56.6	6	"	"	1.4976	67.1
	5	54.6	8	"	"	1.4966	67.7
	6	52.6	10	"	"	1.4939	68.0
17-5	1	57.6	0	"	5	1.5051	64.5
	2	55.6	2	"	"	1.4978	65.7
	3	53.6	4	"	"	1.4933	65.9
	4	51.6	6	"	"	1.4881	66.4
	5	49.6	8	"	"	1.4858	67.2
	6	47.6	10	"	"	1.4818	66.6
17-10	1	52.6	0	"	10	1.4990	64.0 A
	2	50.6	2	"	"	1.4902	64.8
	3	48.6	4	"	"	1.4839	65.0
	4	46.6	6	"	"	1.4791	65.2
	5	44.6	8	"	"	1.4757	65.4
	6	42.6	10	"	"	1.4724	65.5
17-15	1	47.6	0	"	15	1.4932	62.5 A
	2	45.6	2	"	"	1.4866	63.0
	3	43.6	4	"	"	1.4782	63.4
	4	41.6	6	"	"	1.4730	64.2
	5	39.6	8	"	"	1.4688	65.0 A
	6	37.6	10	"	"	1.4680	64.1

(2) Effect of Alumina

A weight percentage substitution of alumina for silica lowers both the index of refraction and the reciprocal dispersion. The figures show that these variations of optical properties with composition are more nearly linear than was the case with fluorine. Exceptions occur when the boric oxide content was too low to permit satisfactory melting and striae elimination so that accurate measurement of the indices of refraction could not be made. The best correlation occurs with relatively high boric oxide content.

The addition of alumina to the batch makes melting more difficult because of the increased viscosity of the melt. In some cases the batch could not be melted as is shown in the first four groups in Tables I and II.

(3) Use of $AlF_3 \cdot 3^1/_2 H_2O$ and KHF_2

Two large-scale melts of identical oxide compositions were made to determine the effect of adding the fluorine either as all KHF_2 or as half KHF_2 and half $AlF_3 \cdot 3^1/_2 H_2O$. Table III gives the results of the two meltings.

Only KHF_2 was used in the experimental melt E-5331 and both KHF_2 and $AlF_3 \cdot 3^1/_2 H_2O$ were used in melt E-6149. The difference in the analyzed fluorine content of the two glasses is not great, but this difference would be anticipated from the slight disagreement in the optical properties of the two glasses. Apparently there is a slightly greater loss of fluorine from the melt when aluminum fluoride is used as a source of fluorine. Offhand, this effect is not the result which might be expected inasmuch as the decomposition temperature of

TABLE II

PERCENTAGE COMPOSITIONS* AND PROPERTIES OF FLUOR-CROWN GLASSES

Glass	No.	SiO_2	F	B_2O_3	Al_2O_3	Index of refraction (N_D)	Reciprocal dispersion $\left(\frac{N_d-1}{N_F-N'}\right)$
5-0-16	1	78.6	0	5	0	1.4900	65.0 A
	2	76.6	2	"	"	1.4877	65.8
	3	74.6	4	"	"	1.4847	66.3
	4	72.6	6	"	"	1.4813	67.0
	5	70.6	8	"	"	1.4789	67.0
	6	68.6	10	"	"	1.4774	67.5
5-5-16	1	73.6	0	"	5	1.492 L	
	2	71.6	2	"	"	1.4912	66.0 A
	3	69.6	4	"	"	1.4839	66.4
	4	67 6	6	"	"	1.4784	67.0
	5	65.6	8	"	"	1.4751	66.9
	6	63.6	10	"	"	1.4729	67.2
5-10-16	1	68.6	0	"	10	1.497 L	
	2	66.6	2	"	"	1.489 L	
	3	64.6	4	"	"	1.478 L	
	4	62.6	6	"	"	1.4708	66.4
	5	60.6	8	"	"	1.4634	67.0
	6	58.6	10	"	"	1.4622	68.0 A
5-15-16	1	63.6	0	"	15		
	2	61.6	2	"	"		
	3	59.6	4	"	"		
	4	57.6	6	"	"	Too viscous to melt down	
	5	55.6	8	"	"		
	6	53.6	10	"	"		
9-0-16	1	74.6	0	9	0		
	2	72.6	2	"	"	1.4970	67.0 A
	3	70.6	4	"	"	1.4915	67.2
	4	68.6	6	"	"	1.4871	68.3
	5	66.6	8	"	"	1.4836	68.2
	6	64.6	10	"	"	1.4821	69.3
9-5-16	1	69.6	0	"	5		
	2	67.6	2	"	"	1.4950	66.0
	3	65.6	4	"	"	1.4850	66.8
	4	63.6	6	"	"	1.4795	67.1
	5	61.6	8	"	"	1.4750	67.3
	6	59.6	10	"	"	1.4727	67.1
9-10-16	1	64.6	0	"	10	1.4971	64.5
	2	62.6	2	"	"	1.4850	65.0 A
	3	60.6	4	"	"	1.4769	65.4
	4	58.6	6	"	"	1.4708	65.8
	5	56.6	8	"	"	1.4652	66.4
	6	54.6	10	"	"	1.4598	66.5
9-15-16	1	59.6	0	"	15		
	2	57.6	2	"	"		
	3	55.6	4	"	"	Too viscous to completely melt; broken from pot; glass batchy	
	4	53.6	6	"	"		
	5	51.6	8	"	"		
	6	49.6	10	"	"	1.4537	65.9

* K_2O, 16.3% throughout; As_2O_3, 0.1% throughout.

aluminum fluoride is so much higher than that of the potassium acid-fluoride. The probable explanation is that KHF_2 enters into the glassforming reactions at a lower temperature than does the $AlF_3 \cdot 3\frac{1}{2} H_2O$ and consequently less fluorine is lost by volatilization.

(4) Boric Oxide in Fluorine-Containing Glasses

Owing principally to the fact that B_2O_3 and SiO_2 have similar optical properties and lie within the fluor-crown field investigated, any substitution of B_2O_3 for SiO_2 had little, if any, effect on optical properties of any of these glasses.

By varying the B_2O_3 content, increased amounts within this field were found to decrease the chemical durability. Although an increase was desirable insofar as ease of melting was concerned, the sacrifice in durabilities was too great. From the standpoint of fusibility, increased fluorine also reduced the viscosity and added to the ease of melting. An optimum balance between B_2O_3 and the F-to-Al_2O_3 ratio was necessary not only from the standpoint of optical porperties, durability, and fusibility but also from that of opalescence. A deliberate decrease was made in B_2O_3 content in a large-scale melt in an attempt to improve the durability. This decrease resulted in higher melting temperature and better durability but immediately introduced an undesirable milky opalescence.

TABLE II (*concluded*)

Glass	No.	SiO_2	F	B_2O_3	Al_2O_3	Index of refraction (N_D)	Reciprocal dispersion $\left(\frac{N_D - 1}{N_F - N_C}\right)$
13-0-16	1	70.6	0	13	0	1.5021	66.4
	2	68.6	2	"	"	1.4978	67.2
	3	66.6	4	"	"	1.4925	67.2
	4	64.6	6	"	"	1.4886	67.8
	5	62.6	8	"	"	1.4856	67.5
	6	60.6	10	"	"	1.4846	67.9
13-5-16	1	65.6	0	"	5	1.4959	66.0 A
	2	63.6	2	"	"	1.4891	66.0
	3	61.6	4	"	"	1.4841	66.1
	4	59.6	6	"	"	1.4786	66.1
	5	57.6	8	"	"	1.4757	66.3
	6	55.6	10	"	"	1.4727	66.7
13-10-16	1	60.6	0	"	10	1.4902	64.0 A
	2	58.6	2	"	"	1.4816	64.5
	3	56.6	4	"	"	1.4754	64.6
	4	54.6	6	"	"	1.4711	65.2
	5	52.6	8	"	"	1.4671	65.6
	6	50.6	10	"	"	1.4626	65.7
13-15-16	1	55.6	0	"	15	Too viscous to melt completely; 1, 2 broken from pot; glass batchy	
	2	53.6	2	"	"		
	3	51.6	4	"	"		
	4	49.6	6	"	"		
	5	47.6	8	"	"	1.4616	64.4
	6	45.6	10	"	"	1.4569	65.5
17-0-16	1	66.6	0	17	0	1.4982	66.0 A
	2	64.6	2	"	"	1.4960	66.7
	3	62.6	4	"	"	1.4913	66.8
	4	60.6	6	"	"	1.4872	67.0
	5	58.6	8	"	"	1.4844	67.5
	6	56.6	10	"	"	1.4833	67.6
17-5-16	1	61.6	0	"	5	1.4927	65.2
	2	59.6	2	"	"	1.4873	66.1
	3	57.6	4	"	"	1.4820	66.1
	4	55.6	6	"	"	1.4786	65.7
	5	53.6	8	"	"	1.4757	65.7
	6	51.6	10	"	"	1.4729	66.0
17-10-16	1	56.6	0	"	10	1.4882	
	2	54.6	2	"	"	1.4810	64.2
	3	52.6	4	"	"	1.4754	64.3
	4	50.6	6	"	"	1.4713	64.7
	5	48.6	8	"	"	1.4682	64.4
	6	46.6	10	"	"	1.4654	65.2
17-15-16	1	51.6	0	"	15		
	2	49.6	2	"	"	1.4763	63.3
	3	47.6	4	"	"		
	4	45.6	6	"	"		
	5	43.6	8	"	"	1.4634	63.9
	6	41.6	10	"	"	1.4611	64.4

TABLE III

RESULTS OF TWO MELTINGS WITH $AlF_3 \cdot 3^1/_2H_2O$ AND KHF_2

Batch oxide compositions		Chemical analyses E-5331	Chemical analyses E-6140
SiO_2	44.1	46.7	46.2
K_2O	16.3	16.7	16.2
F	9.0	7.3	6.7
B_2O_3	15.0	14.7	15.3
Al_2O_3	15.5	15.9	16.0
As_2O_3	0.1		
	100.0	101.3	100.4
N_D		1.4567	1.4573
V		66.0	65.8

(5) Chemical Durability of Fluor-Crown Glasses

The chemical durability of the experimental fluor-crown glasses corresponds roughly to that of the dense barium crowns, which have the poorest durability of all the optical glasses.

An increase of alkali, boric oxide, or fluorine decreases the chemical durability, and silica or alumina improves it. The alkali and boric oxide content was kept as low as possible, but relatively large amounts had to be introduced to permit complete and satisfactory melting of the batch and also to decrease the tendency to form an opalescent glass.

(6) Expansion Curve of Production Melt

The expansion of the production fluor-crown glass, as

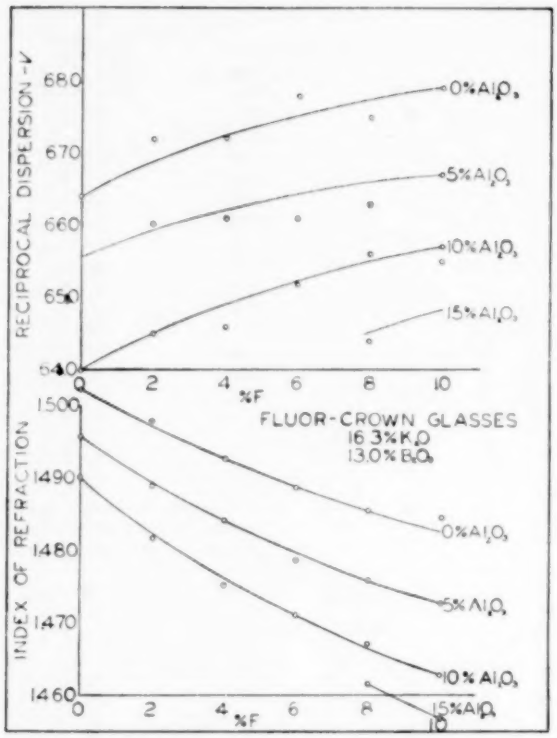


FIG. 8.—Composition versus optical properties of fluor-crown glasses containing 16.3 K_2O and 13.0 B_2O_3.

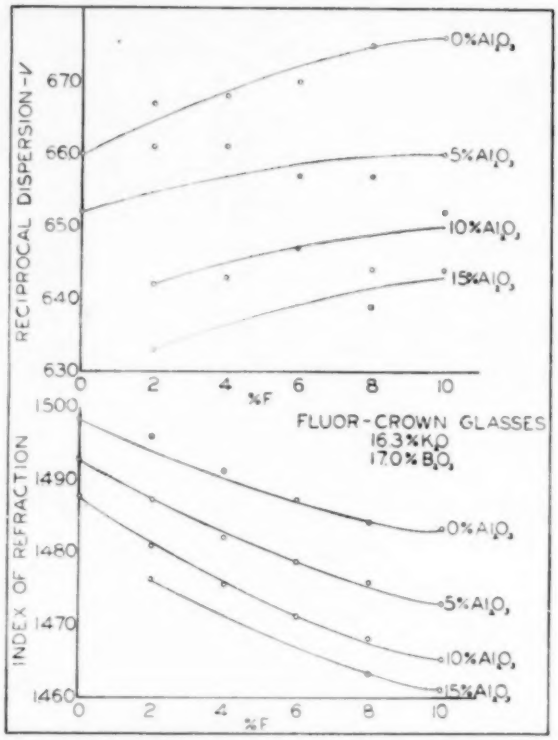


FIG. 9.—Composition versus optical properties of fluor-crown glasses containing 16.3 K_2O and 17.0 B_2O_3.

determined on an interferometer-type dilatometer, is shown in Fig. 10. There is nothing unusual about this glass except the low softening temperature and critical range.

(7) Specific Gravities

A study of the variation of specific gravities with composition was not undertaken. Specific gravities of several glasses were determined, and the majority of them lie between 2.2 and 2.4; the specific gravity of the production melt was 2.311.

IV. Summary

(1) The substitution of fluorine for silica on a weight percentage basis lowers the index of refraction and raises the reciprocal dispersion.

(2) When alumina replaces silica on a weight percentage basis, the index of refraction and also the reciprocal dispersion are lowered.

(3) By changing the ratio of the fluorine and alumina, it is possible to obtain almost any desired optical properties within this fluor-crown field investigated, that is, with an index of refraction of 1.46 to 1.50 and a reciprocal dispersion of 63 to 70.

(4) Boric oxide replacement of silica on a weight percentage basis has little effect on the optical properties, but a sufficient quantity is necessary to permit satisfactory melting and to prevent the formation of an opalescent glass. Substitution of boric oxide, however, lowers the chemical durability and a compromise must be made between satisfactory melting and chemical durability.

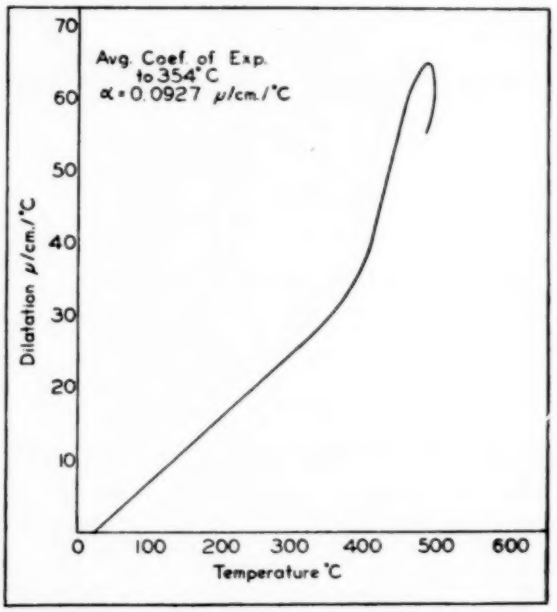


FIG. 10.—Thermal expansion of a production fluor-crown glass.

BAUSCH & LOMB OPTICAL COMPANY
ROCHESTER, NEW YORK

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Two Thousand and Sixty-Four Industrial Laboratories
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Have Enlarged Financing and Activities
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